

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 02-11-2004		2. REPORT TYPE Final Report		3. DATES COVERED (From – To) 17-Sep-01 - 17-Sep-04	
4. TITLE AND SUBTITLE Study of Optoelectronics Properties of Anisotropic Semiconductor Compounds with Ordered Stochiometric Vacancy			5a. CONTRACT NUMBER ISTC Registration No: 2008p		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Professor Iouri Roud			5d. PROJECT NUMBER		
			5d. TASK NUMBER		
			5e. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Ioffe Institute 26 Polytekhnicheskaya St Petersburg 194021 Russia				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0014				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) ISTC 00-7038	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This report results from a contract tasking Ioffe Institute as follows: The main aim of the project is to carry out basic research on optoelectronic properties of CdGeAs ₂ and (Zn,Cd,Hg)(Ga,Al,In) ₂ (S,Se,Te) ₄ materials and to supply samples of these materials to the US AFRL/ML. This research include measurements of X-ray diffraction as well as spectra of polarized first- and second-order Raman scattering by lattice vibrations, photoconductivity, and photoluminescence measurements in a temperature range 77-300K mainly on the crystallographically oriented CdGeAs ₂ , CdGa ₂ S ₄ and HgGa ₂ S ₄ single crystals - the most important representatives of these compounds. Results of these joint investigations will allow the research community to gain a new understanding of the crystalline structure and spectroscopic characteristics of the lattice perfection of these anisotropic group II-IV-V ₂ and II-III ₂ -VI ₄ semiconductor compounds with ordered stochiometric vacancy. These materials will find uses as harmonic generators and tunable lasers in the infrared region of the spectrum.					
15. SUBJECT TERMS EOARD, Physics, Solid State Physics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 56	19a. NAME OF RESPONSIBLE PERSON DONALD J SMITH
a. REPORT UNCLAS	b. ABSTRACT UNCLAS	c. THIS PAGE UNCLAS			19b. TELEPHONE NUMBER (Include area code) +44 (0)20 7514 4953

ISTC 2008p

**Final
Project Technical Report
of ISTC 2008p**

**Study of Optoelectronic Properties
of Anisotropic Semiconductor Compounds
With Ordered Stoichiometric Vacancy**

(From 1 September 2001 to 31 August 2004 for 36 months)

Rud' Yurii Vasil'evich

(Project Manager)

**Ioffe Physico-Technical Institute
RAS**

August 2004

**This work was supported financially by EOARD and performed under the contract to the
International Science and Technology Center (ISTC), Moscow.**

Study of Optoelectronic Properties of Anisotropic Semiconductor Compounds

With Ordered Stoichiometric Vacancy

(From 1 September 2001 to 31 August 2004 for 36 months)

Rud' Yurii Vasil'evich
(Project Manager)

Ioffe Physico-Technical Institute*
RAS

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy

Keywords: anisotropic semiconductors, inelastic light scattering spectra, photoluminescence, photoconductivity, natural palechroism.

* Ioffe Physico-Technical Institute, 26 Polytekhnicheskaya, 194021, St Petersburg
Russia
Phone +7-(812) 247-9140, Fax +7-(812) 247-1017

E-mail: bairamov@mail.ioffe.ru

I. PROJECT ACTIVITIES REPORT

1. Objectives of the Project

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy

2. Scope of Work and Technical Approach

We have grown and selected by preliminary optical and electrical measurements the high quality CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs_2 crystals and in a temperature range from 77 to 300 K on the CdGa_2S_4 and HgGa_2S_4 single crystals.

We have performed also measurements of polarized luminescence spectra on the CdGa_2S_4 and HgGa_2S_4 crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector E_{rad} and tetragonal axis of the crystal c .

We have performed measurements of the temperature dependent polarized photoconductivity spectra on the CdGa_2S_4 and HgGa_2S_4 crystals with n-type conductivity.

We have performed also investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n- CdGa_2S_4 and In-n- HgGa_2S_4 in the temperature range 77-300K.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of CdGeAs_2 grown by low temperature crystallization

3. Summary of Project Technical Report (about 5 to 10 pages)

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs_2 crystals and in a temperature range from 77 to 300 K on the CdGa_2S_4 and HgGa_2S_4 single crystals. All samples were oriented by x-ray measurements. The Raman scattering spectra have been measured for CdGeAs_2 single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature $E_g = 0.57$ eV for CdGeAs_2) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. Excitation of the spectra for CdGa_2S_4 samples were performed

ISTC 2008p

by $\lambda = 514.5$ nm of argon laser and $\lambda = 632.8$ nm of He-Ne laser. The polarization vectors of the incident and scattered light were directed along $[110]$ (\perp) and $[112]$ (\parallel) for the parallel ($e_i \parallel e_s$) ($\perp\perp$) or crossed ($e_i \perp e_s$) ($\perp\parallel$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 nm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have shown that photoluminescence for the CdGa_2S_4 and HgGa_2S_4 crystals in the impurity spectral range for the temperature range 77-300 K is dominant at E_{rad} II c , i.d. with the same polarization configuration, for which dominant absorption takes place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

We have performed measurements of polarized luminescence spectra on the CdGa_2S_4 and HgGa_2S_4 crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector E_{rad} and tetragonal axis of the crystal c . The same type of dependencies was observed for the coefficients of optical absorption for CdGa_2S_4 compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have performed measurements of the temperature dependent polarized photoconductivity spectra on the CdGa_2S_4 and HgGa_2S_4 crystals with n-type conductivity. The spectral dependencies of native photopleochroism coefficient P_N were determined when the temperature is reduced below 300 K.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n- CdGa_2S_4 and In-n- HgGa_2S_4 in the temperature range 77-300K.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of CdGeAs_2 grown by low temperature crystallization

4. Presentation of project results

- List of published reports
 1. Annual Report, Project # 2008p, For 1 year (1 September 2001 – 31 August 2002).
 2. Annual Report, Project # 2008p, For 2 year (1 September 2002 – 31 August 2003).
 3. Final Report, Project # 2008p, For 3 year (1 September 2001 – 31 August 2004).

SUMMARY OF FINAL REPORT

Project # 2008p

1. Title of the Project / Final Report

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy

For 3 years

2. Contracting Institute

Ioffe Physico-Technical Institute
26 Polytekhnicheskaya
194021
St Petersburg
Russia

3. Participating Institutes

4. Project Manager

Rud' Yurii Vasil'evich
26 Polytekhnicheskaya
194021
St Petersburg
Russia
Tel: +7 (812) 247 9140
+7 (812) 247 9915
Fax: +7 (812) 247 1017
E--mail: bairamov@mail.ioffe.ru

5. Commencement Date, Duration

1 September 2001, 3 years

6. Objectives of the Project

Promoting integration of scientists of CIS states into the international scientific community;

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy

7. Scope of Work and Technical Approach

We have grown and selected by preliminary optical and electrical measurements the high quality CdGeAs₂, CdGa₂S₄ and HgGa₂S₄ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs₂ crystals and in a temperature range from 77 to 300 K on the CdGa₂S₄ and HgGa₂S₄ single crystals. The Raman scattering spectra have been measured for CdGeAs₂ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature $E_g = 0.57$ eV for CdGeAs₂) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the c -axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (\perp) and [112] (\parallel) for the parallel ($\mathbf{e}_i \parallel \mathbf{e}_s$) ($\perp\perp$) or crossed ($\mathbf{e}_i \perp \mathbf{e}_s$) ($\perp\parallel$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have performed measurements of polarized luminescence spectra on the CdGa₂S₄ and HgGa₂S₄ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal c . The same type of dependencies was observed for the coefficients of optical absorption for CdGa₂S₄ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation $\tau = 19\%$ and 14% for CdGa₂S₄ and HgGa₂S₄ crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III₂-VI₄ compounds with ordered stoichiometric vacancy.

We have shown that photoluminescence for the CdGa₂S₄ and HgGa₂S₄ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\mathbf{E}_{rad} \parallel \mathbf{c}$, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

To solve the problem of detection low-level signals we have installed new photomultiplier tube with the InP/InGaAs photocathode (for spectral range 300 - 1700 nm), together with the new cooling system required for the tube (up to $T = -200^\circ\text{C}$) as well as an electronics for two-channel single photon counting system, developed and fabricated by us.

8a. Technical Progress

We have grown and selected by preliminary optical and electrical measurements the high quality CdGeAs₂, CdGa₂S₄ and HgGa₂S₄ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs₂ crystals and in a temperature range from 77 to 300 K on the CdGa₂S₄ and HgGa₂S₄ single crystals. The Raman scattering spectra have been measured for CdGeAs₂ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature $E_g = 0.57$ eV for CdGeAs₂) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the c -axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (\perp) and [112] (\parallel) for the parallel ($\mathbf{e}_i \parallel \mathbf{e}_s$) ($\perp\perp$) or crossed ($\mathbf{e}_i \perp \mathbf{e}_s$) ($\perp\parallel$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have performed measurements of polarized luminescence spectra on the CdGa₂S₄ and HgGa₂S₄ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal c as well as we. The same type of dependencies was observed for the coefficients of optical absorption for CdGa₂S₄ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation $\tau = 19\%$ and 14% for CdGa₂S₄ and HgGa₂S₄ crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III₂-VI₄ compounds with ordered stoichiometric vacancy.

We have shown that photoluminescence for the CdGa₂S₄ and HgGa₂S₄ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $\mathbf{E}_{rad} \parallel c$, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

Polarization dependent measurements of the photoconductivity spectra has been performed on the CdGa₂S₄ and HgGa₂S₄ crystals, for the first time. These measurements were conducted with shining along the normal to (100) and (001) faces of the CdGa₂S₄ and HgGa₂S₄ crystals, that allowed to determine the coefficient of the photopleochroism. Obtained results allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The photoconductivity spectra I^{\parallel} and I^{\perp} have maximum at $\hbar\omega^m = 2.23$ eV for HgGa₂S₄ and $\hbar\omega^m = 2.76$ for CdGa₂S₄ which are essentially less then the band gap of these semiconductors. Therefore, the observed spectra can be attributed to the photoactive absorption with participation of lattice defects, located at the activation energies $E_D \approx 0.6$ eV (for HgGa₂S₄) and ≈ 0.8 eV (for CdGa₂S₄). The photoconductive bands in these crystals can be characterized also by full width at the

half maximum $\delta \approx 0.38$ eV (for CdGa₂S₄) and $\delta \approx 0.4$ eV (for HgGa₂S₄). Large values of δ as well as the bands asymmetry with long-wavelength tailing indicate on nonelementarily and, therefore, on the complex energetic spectra of the lattice defects of the crystals under the study. We show that in this group of the crystals with defect chalcopyrite structure exist phenomenon of native photopleochroism and azimuthal dependencies of photoconductivity in agreement with the crystalline symmetry of these compounds.

Our measurements of the photoconductivity spectra of CdGa₂S₄ and HgGa₂S₄ compounds oriented in the (100) plane show that native photopleochroism coefficient in these crystals has additional sign in the range of the maximum of the photoconductivity and the maximum value of $P_N \approx 20\%$ for HgGa₂S₄ crystals and $P_N \approx 10\%$ for CdGa₂S₄.

It is important to note that we observe also strict decreases of the amplitude of P_N and an inversion of its sign in the range of the strict cut-off of the photoconductivity. The reason of such inversion can be connected as with the increase of the surface recombination velocity as well as with changing the selections rules with the changing of the incident photon energy in the range of strong interband absorption. For final selection between these possibilities it is need further study of interconnections of the polarization photoconductivity measurements and technological aspects of the growth processes of these ternary compounds.

Our study of the azimuthal dependencies of photoconductivity i_ϕ of the CdGa₂S₄ and HgGa₂S₄ single crystals allow to establish that the positive native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane. The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axisies [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the HgGa₂S₄ CdGa₂S₄ single crystals.

Our experimental search was also devoted toward study of electrical properties and optical absorption of the HgGa₂S₄ single crystals, study of contact properties of these crystals with some metals with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion.

We established that mechanical contact of pure metal layers of (In, Ni, Au, Ag) with the cleaved surface of the HgGa₂S₄ single crystals and further with chemically polished surface of electrically homogeneous HgGa₂S₄ give rectifying characteristics. Rectification determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 20$ V, reaches the values $K \approx 200$, that is the record value obtained up to now for the the *n*-HgGa₂S₄ single crystals. We find that direct and reverse current-voltage characteristics in the case of illumination shifts relatively darks in the direction of increasing direct and reverse currents. We show the real way of further improvement of the surface-barrier structure characteristics on the base of HgGa₂S₄ with solving size and crystal perfection problems.

We find that photovoltage of the free motion in the surface-barrier structures on the base of n -HgGa₂S₄ single crystals is dominated under conditions of illumination of the structures from the side of barrier contacts. In this case the sign of the photovoltage always corresponds to the direction of the rectification in the structures and independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. These established facts on the structures obtained for the first time can be used as a base to connect rectification and photovoltaic effect with energy barrier at the contact of semiconductor with metal studied. Maximum value of the voltage photosensitivity achieved for the surface-barrier In- n -HgGa₂S₄ structures is $2 \cdot 10^3$ V/W at $T=300$ K.

We have measured spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier In- n -HgGa₂S₄ structures. It is found that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 0.8-3.8 eV. It is shown that the spectral parameter η at $\hbar\omega < 2.2$ eV strongly changes from structure to structure and may be used for the diagnostic of the material perfection. Under condition of illumination of from the substrate side at the photon energy range $\hbar\omega > 2.25$ eV in the η spectra appears sharp cut-off of the photosensitivity. This cut-off may indicate on increase of the optical absorption in the HgGa₂S₄ plate. It can be supposed that due to small length of a diffusion shift of the nonequilibrium charge carriers the concentration of the photogenerated carriers, which achieve the active area, with increasing the photon energy $\hbar\omega > 2.3$ eV begin to fall and, therefore, the quantum efficiency of photoconversion $\eta \rightarrow 0$. It is important to note that the cut-off spectral range of η under the condition of illumination of Shottky barriers from the substrate side is in an agreement with a beginning of sharp increase of the optical absorption coefficient α exactly at photon energy $\hbar\omega \approx 2.3$ eV. This value can be used as a preliminary estimation of the absorption edge E_G of this little known semiconductor. We show that the $\eta(\hbar\omega)$ spectra in the range of $\hbar\omega < 2.25$ eV are practically independent on illumination geometry of the surface-barrier structures that is due to the bulk nature of the charge carrier photogeneration in the HgGa₂S₄ crystals. The longwavelength edge of the photosensitivity of the surface-barrier structures in the range of $\hbar\omega < 2.2$ eV follows to the Fowler law and, therefore, is rectified in the coordinates $(\eta\hbar\omega)^{1/2} - \hbar\omega$. From the extrapolation of the direct linear parts $\eta^{1/2} \rightarrow 0$ we obtain first estimation of the energy height of In- n -HgGa₂S₄ and Ag- n -HgGa₂S₄ structures $\phi_D \approx 1.1$ eV at $T=300$ K. We note, that for some barriers in the dependencies $(\eta\hbar\omega)^{1/2} - \hbar\omega$ revealed several direct linear parts and, correspondingly, several cut-off energies. This situation may reflect complicated nature of the energy band structure of the HgGa₂S₄ crystals.

The increase of the photoconductivity in the best surface-barrier structures at $\hbar\omega > 2.3$ eV under the condition of illumination of the structures from the barriers side can be related with the fundamental absorption in the HgGa₂S₄ crystals, that is not possible to detect by traditional absorption spectroscopy techniques on such a small size samples. We find that the increase of the photoconductivity in the best surface-barrier structures at the photon energy range of 2.3-2.8 eV follows the $(\eta\hbar\omega)^{1/2} - \hbar\omega$ law. Extrapolation of this dependence $(\eta\hbar\omega)^{1/2} \rightarrow 0$ allows to estimate the energy of indirect interband optical transitions $E_G^{in} \approx 2.27$ eV for n -HgGa₂S₄ at $T=300$ K. More sharp increase of the photoconductivity in the surface-barrier structures at the photon energy range of $\hbar\omega > 2.8$ eV follows to the characteristic for the direct optical transitions quadratic $(\eta\hbar\omega)^2 - \hbar\omega$ law. Extrapolation of this dependence $(\eta\hbar\omega)^2 \rightarrow 0$ allows to estimate the

energy of direct interband optical transitions $E_G^{dir} \approx 2.86$ eV for n -HgGa₂S₄ at $T=300$ K. So, in this work for the first time, the problem of creation of the photosensitive structure on the base of n -HgGa₂S₄ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of n -HgGa₂S₄ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

We have performed investigations of the contact phenomena of photosensitive surface-barrier structures on the base of the CdGa₂S₄ single crystals with n-type conductivity. We study the stationary and light current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion in dependence of the geometry of excitation with a unpolarized irradiation.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-CdGa₂S₄ and In-n-HgGa₂S₄ in the temperature range 77-300K.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of CdGeAs₂ grown by low temperature crystallization.

9a. Plan for Following Year(s) (in the case the original work plan has been significantly changed)

10a. References of papers and reports published.

1. Annual Report, Project # 2008p, For 1 year (1 September 2001 – 31 August 2002).
2. Annual Report, Project # 2008p, For 2 year (1 September 2002 – 31 August 2003).
3. Final Report, Project # 2008p, For 3 year (1 September 2001 – 31 August 2004).

FINAL TECHNICAL REPORT

1. Title of the Project / Number of Final Report

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy

For 3 years

2. Contracting Institute

Ioffe Physico-Technical Institute
26 Polytekhnicheskaya
194021
St Petersburg
Russia

3. Participating Institutes

4. Project Manager, phone number, fax number, e-mail address

Rud' Yurii Vasil'evich
26 Polytekhnicheskaya
194021
St Petersburg
Russia
Tel: +7 (812) 247 9140
+7 (812) 247 9915
Fax: +7 (812) 247 1017
E--mail: bairamov@mail.ioffe.ru

5. Commencement Date, Duration

1 September 2001, for 3 years

6a. Brief description of the work plan: objective, expected results, technical approach

The main aim of the project is to carry out basic research on study of optoelectronic properties of anisotropic semiconductor compounds CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 with ordered stoichiometric vacancy.

According to the Work Plan we have conducted:

Task 1

Standard x-ray diffraction measurements on the CdGeAs_2 , CdGa_2S_4 and HgGa_2S_4 crystals, for determination homogeneity and the crystallographic orientation of the samples.

Task 2

Measurements of polarized Raman scattering by phonons (at room temperature on the CdGeAs_2 and in a temperature range from 77 to 300 K on the CdGa_2S_4 and HgGa_2S_4)

for accomplishment the Raman selection rules, for determination symmetry and spectroscopic parameters (frequencies, linewidth, intensities) of phonon lines,

Task 3

Polarized photoluminescence measurements (on CdGa₂S₄ and HgGa₂S₄) in a temperature range from 77 to 300 K.

Task 4

Polarized photoconductivity measurements (on CdGa₂S₄ and HgGa₂S₄) in a temperature range from 77 to 300 K.

Task 5

Polarized photosensitivity measurements (in a temperature range from 77 to 300 K) of surface barriers on In/CdGa₂S₄ and In/HgGa₂S₄.

Task 6

Temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements for determination mobility, concentration, activation energy of impurity level, and degree of compensation,

We have grown and selected by preliminary optical and electrical measurements the high quality CdGeAs₂, CdGa₂S₄ and HgGa₂S₄ samples, which were crystallographically oriented by using x-ray measurements.

We have performed measurements of polarized Raman scattering spectra by optical phonons at room temperature on the CdGeAs₂ crystals and in a temperature range from 77 to 300 K on the CdGa₂S₄ and HgGa₂S₄ single crystals. The Raman scattering spectra have been measured for CdGeAs₂ single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature $E_g = 0.57$ eV for CdGeAs₂) these measurements have been performed in the back-scattering configuration. The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the c -axis of the crystal was 54.7°. The polarization vectors of the incident and scattered light were directed along [110] (\perp) and [112] (\parallel) for the parallel ($\mathbf{e}_i \parallel \mathbf{e}_s$) ($\perp\perp$) or crossed ($\mathbf{e}_i \perp \mathbf{e}_s$) ($\perp\parallel$) polarizations of the incident and scattered light, respectively. We have observed in the spectral range 80-400 1/cm 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

We have performed measurements of polarized luminescence spectra on the CdGa₂S₄ and HgGa₂S₄ crystals in a temperature range from 77 to 300 K and observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal c as well as we. The same type of dependencies was observed for the coefficients of optical absorption for CdGa₂S₄ compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions.

We have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation $\tau = 19\%$ and 14% for CdGa₂S₄ and HgGa₂S₄ crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α

which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III₂-VI₄ compounds with ordered stoichiometric vacancy.

We have shown that photoluminescence for the CdGa₂S₄ and HgGa₂S₄ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at E_{rad} II c, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

To solve the problem of detection low-level signals we have installed new photomultiplier tube with the InP/InGaAs photocathode (for spectral range 300 - 1700 nm), together with the new cooling system required for the tube (up to T = - 200°C) as well as an electronics for two-channel single photon counting system, developed and fabricated by us.

7a. Technical progress during the 1 year of reference

- compliance with tasks and milestones as described in the work plan

All works are on schedule.

- achievements of the first year

Multicomponent anisotropic semiconductor II-IV-V₂ (CdGeAs₂) and II-III₂-VI₄ (Zn,Cd,Hg)(Ga,Al,In)₂(S,Se,Te)₄ compounds with ordered stoichiometric vacancy known as chalcopyrites and defect chalcopyrites or thiogallates, respectively. The most important representatives of these compounds are CdGeAs₂, CdGa₂S₄ and HgGa₂S₄.

The chalcopyrite structure CdGeAs₂ crystals have the symmetry with space group $D_{2d}^{12}(I\bar{4}2d)$ and the body centered tetragonal unit cell.

Single crystals of chalcopyrite type CdGeAs₂ have been grown by the improved low temperature directional crystallization technique from non-stoichiometric melts. This technique allows to grow crystals at the temperature range significantly below the temperature of chalcopyrite \rightarrow sphalerite phase transition (~ 870 K). This situation may allow to perform crystallization of CdGeAs₂ compounds in the range of stability of the chalcopyrite structure, when the formation of the equilibrium sphalerite structure is forbidden. Therefore drastically decrease of deviation from the stoichiometry by minimizing concentration of Cd_{Ge} and Ge_{Cd} antisite defects should be achieved.

The defect chalcopyrites or thiogallates structure CdGa₂S₄ and HgGa₂S₄ crystals have the symmetry with space group $S_4^2(I\bar{4})$ with two formula units in the cell. There are no data in literature on the phase transition in the CdGa₂S₄ and HgGa₂S₄ crystals. Hence the question of formation of the antisite defects in these crystals remains open.

Therefore before starting the time-consuming x-ray measurements for crystallographic orientation of the CdGeAs₂, CdGa₂S₄ and HgGa₂S₄ samples, we have made preliminary mapping measurements, by using all of our planned

experimental techniques to select high optical quality and homogeneity areas of the grown crystals. We performed such measurements of the optical absorption, photoelectric, photoluminescence and Raman scattering spectra, which allowed selecting high quality samples for our further measurements.

Our X-ray diffraction measurements have been carried out by employing the typical diffractometer DRON-2, equipped with the four-ring goniometer GUR- 5. The radiation source was MoK_α radiation. Monochromatization was achieved by using a pyrolytic graphite crystal.

For the CdGeAs_2 crystal we have found 6 crystallographic orientation, of as-grown surfaces, corresponding to (112), (112-), (101), (101-), (110) and (11-0). To monitor the body centered tetragonal unit cell of the CdGeAs_2 we found the following values for the parameters of the unit cell: $a = (5.9403 \pm 0.0002) \text{ \AA}$ and $c = (11.2022 \pm 0.0005) \text{ \AA}$. One of the main structural parameter, characteristic for the chalcopyrite type compounds is tetragonal compression $h = (1 - c/2a)$, which deviates parameter c from the ideal ratio $c = 2a$. This value is very close to $h = 1$ among all chalcopyrite type compounds. In our case $h = 0.0571$ in good agreement with the literature data.

For the sample cut from the CdGa_2S_4 crystal the orientation of the sample on the main crystallographic surfaces (100), (001) and (010) was determined by using the following reflections found: 325, 215, 224, 226 and 316. For the determination of the parameters of unit cells the following reflections were used: 0.0.24, 14.0.0, 10.10.0, 10.0.20, 0.0.28 and 14.6.0. The following values for the parameters of the unit cell: $a = (5.5460 \pm 0.0003) \text{ \AA}$ and $c = (10.1654 \pm 0.0005) \text{ \AA}$, which are also in good agreement with the literature data.

Task 2:

The chalcopyrite structure CdGeAs_2 crystals have the symmetry with space group $D_{2d}^{12} (I\bar{4}2d)$ and the body centered tetragonal unit cell with two formula units and, therefore, eight atoms. Therefore, there are 21 optical and 3 acoustical lattice vibrational branches with with the following representation for the Brillouin zone center with $k=0$

$$\Gamma = 1\Gamma_1 + 2\Gamma_2 + 3\Gamma_3 + 3\Gamma_4 + 6\Gamma_5 \quad \text{и} \quad 1\Gamma_4 + 1\Gamma_5.$$

With the splitting of infrared active modes Γ_4 and Γ_5 by the macroscopic long range electrostatic interaction into transverse and longitudinal components as well as taking into account that the Γ_2 modes are silent, one expects 22 Raman-active optical modes:

$$1\Gamma_1 + 3\Gamma_3 + 3\Gamma_4(\text{LO}) + 3\Gamma_4(\text{TO}) + 6\Gamma_5(\text{LO}) + 6\Gamma_5(\text{TO}).$$

The Raman scattering spectra have been measured for CdGeAs_2 single crystals at room temperature by using the two argon laser lines at 488.0 and 514.5 nm. Due to the small value of the direct gaps (at room temperature $E_g = 0.57 \text{ eV}$ for CdGeAs_2) these measurements have been performed in the back-scattering configuration.

The laser beam was directed perpendicular to the (112) crystallographic plane. The angle between the direction of phonon propagation and the c -axis of the crystal was 54.7° . The polarization vectors of the incident and scattered light were directed along [110] (\perp) and [112] (\parallel) for the parallel ($\mathbf{e}_i \parallel \mathbf{e}_s$) ($\perp\perp$) or crossed ($\mathbf{e}_i \perp \mathbf{e}_s$) ($\perp\parallel$) polarizations of the incident and scattered light, respectively.

For the both polarizations at the room temperature, corresponding spectra were also obtained for the anti-Stokes components of these spectra. This fact indicate that the all observed sharp lines are caused by the first-order Raman light scattering by optical phonons corresponding to the center of the Brillouin zone.

All these spectra also demonstrate clear polarization dependence and indicate that the vibrational modes are anisotropic. Moreover, the properly polarization behavior of the Raman scattering spectra obtained from the long-wavelength optical phonons and the sharpness of the lines with the deconvoluted values of full width at half intensity of 1-3 cm^{-1} as well as absence of background scattering indicated on high crystalline quality of the grown CdGeAs₂ single crystals.

In addition, the mapping measurements taken with a step of 0.3 mm showed a high reproducibility of all parameters of the spectra (scattering intensity, frequency shift, line width and polarization). These observations also indicate high homogeneity of the grown crystals.

The following measured frequencies (in cm^{-1}) together with the results of our interpretation of the symmetry of the all observed zone-center optical phonons are for CdGeAs₂ single crystals have been obtained:

$$\begin{aligned} 66 &- \Gamma_5(\text{TO}); \\ 78 &- \Gamma_4(\text{TO}); \\ 94 &- \Gamma_4(\text{LO}); \\ 161 &- \Gamma_5(\text{LO}); \\ 193 &- \Gamma_1; \\ 202, 273, \text{ and } 283 &- \Gamma_5(\text{LO}). \end{aligned}$$

The defect chalcopyrites or thiogallates structure CdGa₂S₄ crystals have the symmetry with space group $S_4^2(I\bar{4})$ with two formula units in the cell.

Such a structure can be considered as obtained from the sphalerite structure by adding ordered vacancies. It is intermediate between CdS, when Cd atoms occupies half of the tetrahedral voices of cubically packed S atoms, and α -Ga₂S₃, when Ga atoms occupies 1/3 of such voices. At the same time Cd and Ga atoms occupies 1/8 and 1/4 of the tetrahedral voices.

There are 7 atoms in the unit cells of the CdGa₂S₄ and HgGa₂S₄ crystals. The vibrational representation at the Γ point ($\kappa = 0$) can be given as

$$\Gamma = 3A + 6B + 6E.$$

These 15 optical modes are polar and Raman-active.

Our Raman measurements on CdGa₂S₄ crystals have been performed on the samples preliminarily crystallographically oriented by x-ray diffraction measurements sample on the main crystallographic surfaces (100), (001) and (010). The scattering spectra were excited at room temperature by using the argon laser line at 514.5 nm and 632.8 nm line of the He-Ne laser.

We have observed in the spectral range 80-400 $1/\text{cm}$ 18 spectral lines. All these lines appeared also in the anti-Stokes components indicating that they are induced by scattering rather than luminescence.

Moreover measurements performed at low temperatures (up to $T=77\text{K}$) indicated that all these lines exhibited small intensity dependence as well as small frequency shifts (in the range 2-3 1/cm) indicating that all these lines corresponds to the first-order scattering by the Brillouin zone center optical phonons. These preliminary results are in good agreement with the infrared absorption data performed on CdGa_2S_4 crystals (V. Slivka et al, UPJ, 22,1951-1953, 1977).

The defect chalcopyrites or thiogallates structure HgGa_2S_4 crystals also have the symmetry with space group $S_4^2(I\bar{4})$ with two formula units in the cell. Similar Raman scattering measurements for these crystals were performed with spectral resolution of 3 cm^{-1} at room temperature by using the argon laser line at 514.5 nm and 632.8 nm line of the He-Ne laser. These measurements have revealed approximately 7 spectral lines. They are located in the spectral range of 60-750 cm^{-1} , namely, at 373, 416, 428, 446, 571, 576, and 750 cm^{-1} in the spectra with the both of excitations used indicating that they induced by the Raman scattering and not luminescence. The most intense lines have been observed also in the anti-Stokes spectra directly indicating that they are due to the optical phonons. There are no literature data on phonons in the HgGa_2S_4 crystals.

Our light scattering spectra for CdGa_2S_4 and HgGa_2S_4 crystals have been obtained by using the analog detection system under the linear scanning on wavelengths, which does not allow to obtain the spectra linear on wavenumber directly. Now we are finishing the works on connecting personal computer that will allow computer-controlled scanning of our double grating spectrometer SDL-1. Moreover, such a system will allow digital registration of the light scattering spectra.

In addition the low sensitivity of our photomultiplier does not allow to detect spectra with high signal/noise ratio. Therefore the full treatment of the obtained experimental data and final results on determination the phonon frequencies and their symmetry identification will be conducted after connecting the new photomultiplier with InP/InGaAs photocathode, Hamamatsu R5509-72 (currently we have purchased such a photomultiplier) and obtaining supplementary spectra which will be possible to process by using computer.

Task 3:

Early the photoluminescence spectra of CdGa_2S_4 compounds were investigated relatively in detail while there is only one publication about HgGa_2S_4 . Polarization dependence for both crystals were not known. It evident that such studies can be interesting for clarification the nature of optoelectronic phenomena in such a multicomponent anisotropic semiconductors.

Photoluminescence was excited by the focused radiation (the excitation spot diameter was approximately 0.1 mm) of the He-Cd laser with excitation energy of $\hbar\omega_{exc} \approx 2.88\text{ eV}$ and density of $P \approx 10^{19}\text{ quant /cm}^2\cdot\text{s}$. Luminescence spectra were detected by using grating monochromator MDR-3 (LOMO) and photomultiplier PhEU-62. The spectral sensitivities of the monochromator and photomultiplier were corrected by the tungsten spectral lump. Spectral resolution was better than 1 meV.

Main results of measured for the first time polarized photoluminescence spectra can be formulated as following:

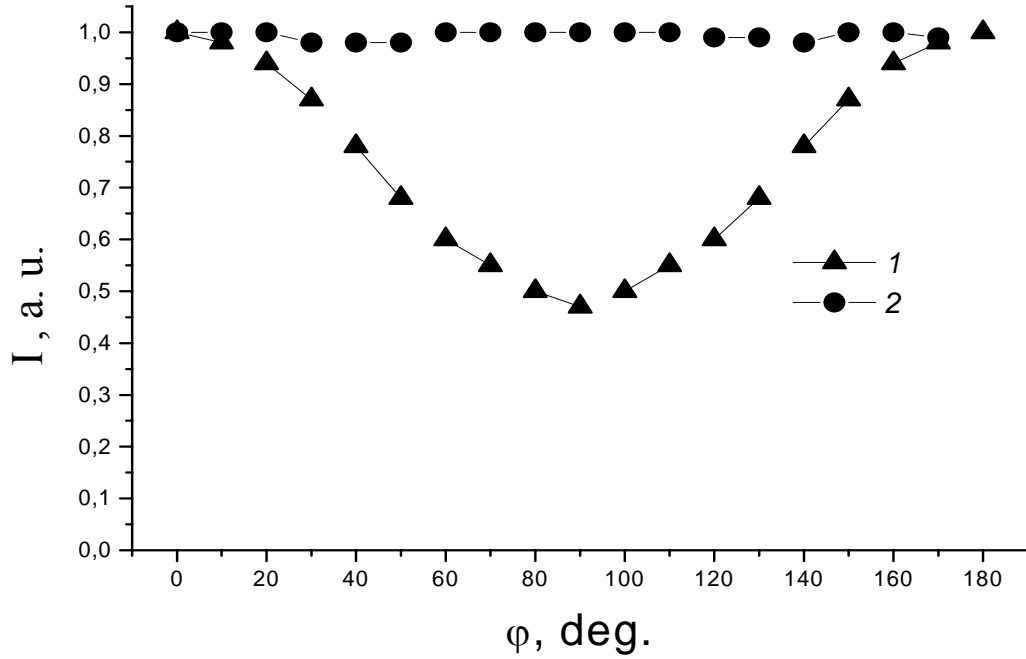


Fig.1. Polarization indicatrics of the PL intensity for CGS at $T = 300$ K.
 $\hbar\omega = 2.0$ eV, Crystallographic directions for registration of the PL:
 curve 1 – [100], curve 2 – [001]. Sample No. 4.

- i) we have observed the dependence of the photoluminescence intensity on the azimuthal angle φ between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal \mathbf{c} . We find that the intensity dependence for the case of registration the radiation along the normal parallel to the (100) and (010) faces in the temperature range 77 – 300 K is described as

$$I_{\varphi} = I^{\parallel} \cos^2 \varphi + I^{\perp} \sin^2 \varphi, \quad (1)$$

where I^{\parallel} and I^{\perp} - are photoluminescence intensities for $\mathbf{E}_{rad} \parallel \mathbf{c}$ and $\mathbf{E}_{rad} \perp \mathbf{c}$, respectively. The same type of dependencies was observed for the coefficients of optical absorption for CdGa_2S_4 compounds oriented along (100) face and for the quantum efficiency of photoconversion for photosensitive structures on their base in the range of the interband transitions. This fact indicates that Kirkhgoff law on detailed correspondence between absorption and radiation processes is fulfilled for this new class of semiconductor materials.

The dependence described by the Eq.1 not shows a sensitivity to the excitation radiation (unpolarized or changing the orientations of \mathbf{E}_{rad} and photon energy $\hbar\omega_{exc}$. Only the rotations of the sample in the (100) and (010) planes that cause the changes of the space orientation of the axis \mathbf{c} , is accompanied by changing the electric field polarization vector of light wave in the photoluminescence spectra.

It is important to note that in the case of registration photoluminescence spectra from (001) plane when tetragonal axes of CdGa_2S_4 compound is collinear to the direction of registration the photoluminescence spectra became isotropic. All deviations of the registration direction from axis \mathbf{c} cause to accomplishment of Kirhof law described by Eq. 1. At same time the ratio of

intensities $I^{\parallel} / I^{\perp}$ at the $\hbar\omega = \text{const}$ reaches the maximum value if the photoluminescence light is analyzed in the directions perpendicular to the collinear axes c .

So, we have shown that observed anisotropy of photoluminescence is determined by the native uniaxial deformation $\tau = 19\%$ and 14% for CdGa_2S_4 and HgGa_2S_4 crystals, respectively, (see Table 1) and that corresponding polarization indicatrise I and α which describe radiation and absorption processes, indicate fulfillment of Kirhof law in multicomponent semiconductor II-III₂-VI₄ compounds with ordered stoichiometric vacancy.

- ii) Spectral dependences of photoluminescence spectra for the CdGa_2S_4 and HgGa_2S_4 crystals in the investigated temperature range have as a rule a form of a broad structureless bands. Table 2 shows typical values of the maximum of photoluminescence band $\hbar\omega^m$ at $T = 300$ and 77 K. These values are lower than the corresponding band gap. Therefore, the recombination radiation of these crystals is determined by transitions of electrons to the deep levels of

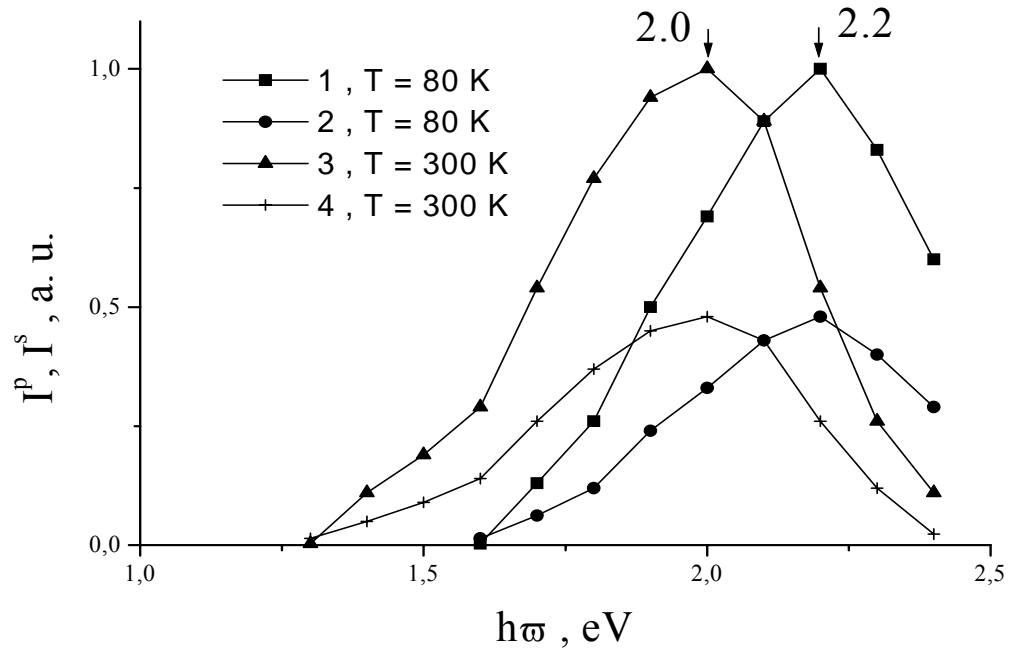


Fig.2. Spectral dependence of the PL intensity for CGS. The direction of the PL detection is $[100]$. Temperature T : for curves 1 and 2 – 80 K, for curves 3 and 4 – 300 K. PL polarizations: cuerves 1 and 3 - $E \parallel C$ (I^p), curves 3 and 4 – $E \perp C$ (I^s). Sample No. 10.

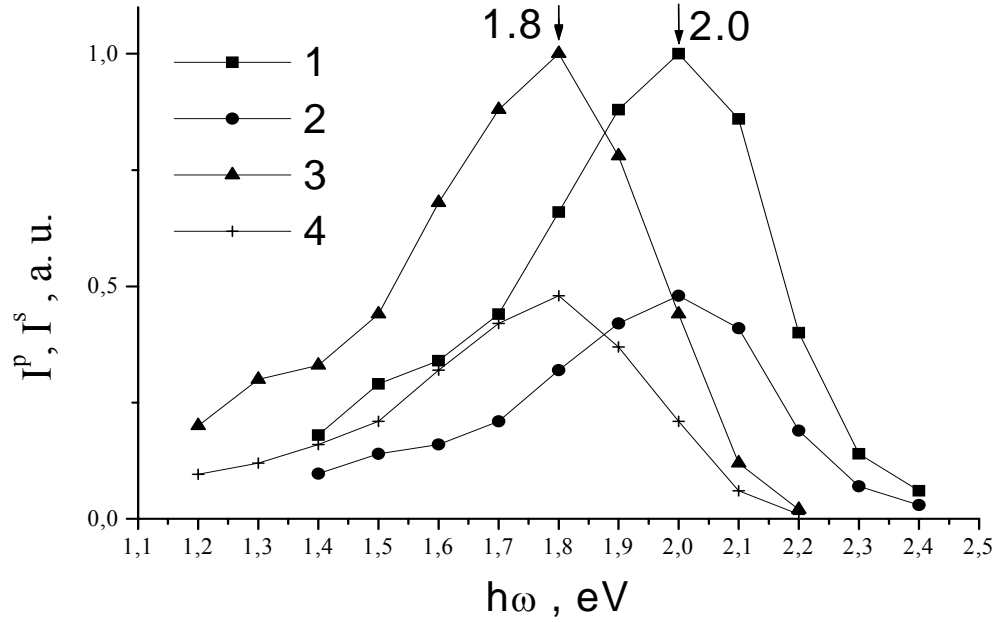


Fig.3. Spectral dependence of the PL intensity for HGS. The direction of the PL detection is [100]. Temperature T: for curves 1 and 2 – 80 K, for curves 3 and 4 – 300 K. PL polarizations: curves 1 and 3 – $E \parallel C$ (I^p), curves 2 and 4 – $E \perp C$ (I^s). Sample No. 6.

antisite defects, which are lower by 0.8 – 1.0 eV than the band gap for the HgGa_2S_4 crystals and by 1.4 – 1.6 eV for the CdGa_2S_4 crystals. Observed shifts for both crystals of the maximum of photoluminescence band to the low wavelength range indicate different contributions of deep levels to the recombination process.

We find that values of full width at half maximum $\delta_{1/2}$ are large that indicate on nonelementar character of recombination transitions. Note that observed broad photoluminescence bands for the CdGa_2S_4 and HgGa_2S_4 crystals are in the range of high optical transparency, when $\hbar\omega^m < E_G$, thus they can be attributed to the recombination transitions with participation of the antisite levels.

With reduction of the excitation energy level, as a role, we find the increase of the long-wavelength contributions that cause the enhancement of the long-wavelength shoulders and red shift of the bands for both crystals. In some crystals we have observed also red shift of $\hbar\omega^m$ also of short-wavelength shoulders. These observations form the base for conclusion that dominated processes are donor-acceptor recombination. Similar behavior of the photoluminescence spectra for both crystals indicate that donor and acceptor components can be related to the point defects in gallium and sulfur sub lattices.

Luminescence spectra emitted from (100) plane showed that the recombination radiation in the temperature range 77 – 300 K are partially polarized and dominated for $E_{rad} \parallel c$ polarization while the shape of the bands for both polarizations $E_{rad} \parallel c$ and $E_{rad} \perp c$ were the same as in the case of chalcopyrite crystals [2]. Therefore, the degree of polarization of the luminescence determined as

$$P = (I^{\parallel} - I^{\perp}) / (I^{\parallel} + I^{\perp}), \quad (2)$$

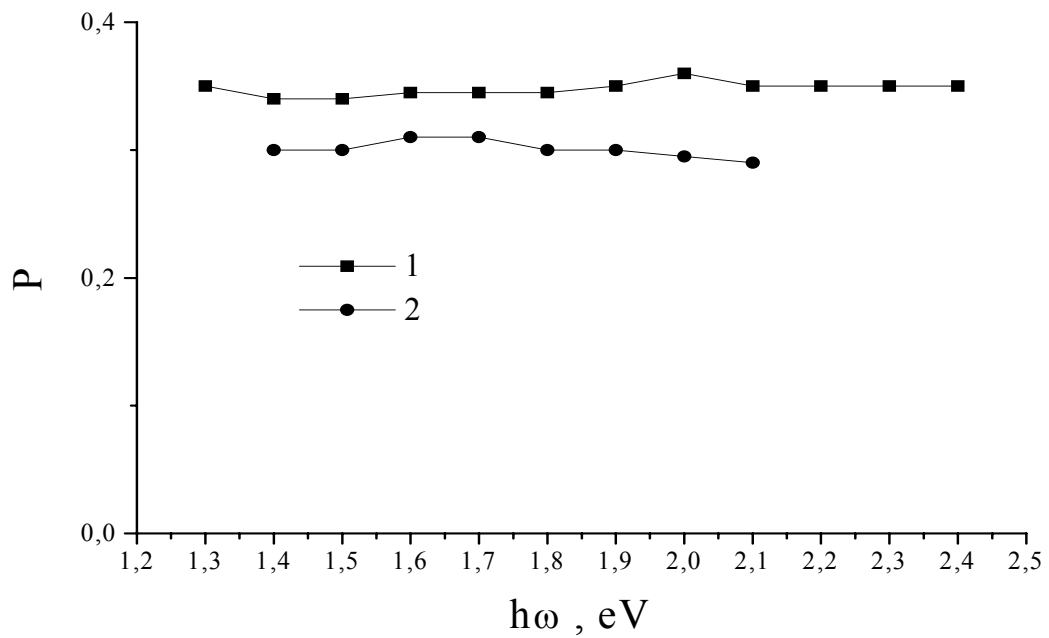
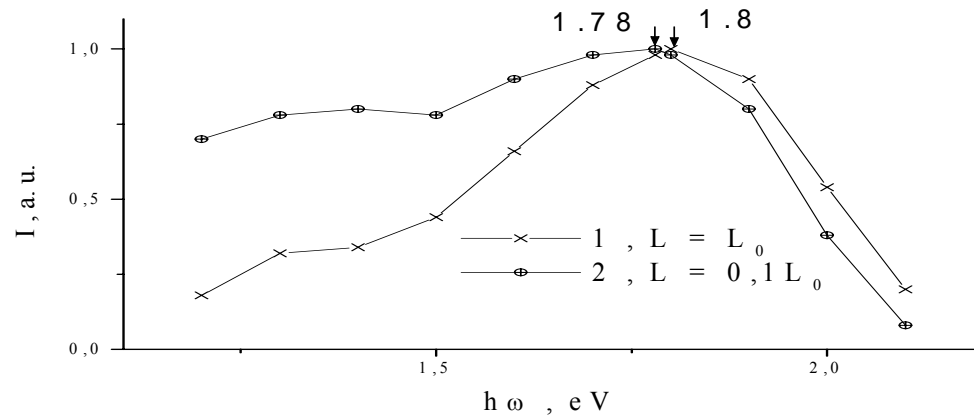


Рис. 4. Dependence of The PL spectra for HGS on en excitation energy. $T = 80$ K, Excitation intensity L/L_0 , in arbitrary units:
1 – 1.0, 2 – 0.1.

became positive $P > 0$ for the CdGa_2S_4 and HgGa_2S_4 crystals. The result is in a good agreement with our polarized measurements of optical absorption coefficient n in the same samples and theoretical calculations of the band gap of the multicomponent anisotropic semiconductors with ordered stoichiometric vacancy [3]. On the base of our polarized measurements the observed photoluminescence bands (Table 2) are connected with radiation transitions with participation of levels induced by Γ_1 and Γ_3 bands.

Fig. 5. Spectral dependence of the linear polarizatio P of PL
for CGS (curve 1, $T = 80$ K) and HGS (curve 2, $T = 300$ K).



The degree of polarization of the photoluminescence bands were practically constant and in addition independent on temperature. This may be the consequence of the high tetragonal deformation of crystalline lattices of these compounds (Table 1) and corresponding high values of the splitting of upper valence bands by the tetragonal crystal fields. Low values and absence of the P dispersion for the CdGa_2S_4 and HgGa_2S_4 crystals in the investigated spectral range is not

unexpected. These data are in agreement with the early-observed reduction of the anisotropy of oscillators, which take place in the case of radiation with participation of deep levels.

Therefore, photoluminescence for the CdGa₂S₄ and HgGa₂S₄ crystals in the impurity spectral range for the temperature range 77-300 K is dominant at $E_{rad} \parallel c$, i.d. with the same polarization configuration, for which dominant absorption take place in the range of direct interband transitions $\Gamma_1 \rightarrow \Gamma_3$ [3].

Table 1.

Physical properties for the CdGa₂S₄ and HgGa₂S₄ crystals at $T = 300$ K.

Compound	Space group	Lattice constants a and c	τ	E_g
			%	eV
HgGa ₂ S ₄	S ₄ ²	5.50 10.23	14	2.8
CdGa ₂ S ₄	S ₄ ²	5.57 10.08	19	3.58

Table 2

Parameters of photoluminescence bands for the CdGa₂S₄ and HgGa₂S₄ crystals

Compound	300 K			77 K		
	$\hbar\omega^m$ eV	$\delta_{1/2}$ eV	P %	$\hbar\omega^m$ eV	$\delta_{1/2}$ eV	P %
HgGa ₂ S ₄	2.0	0.45	0.3	1.8	0.4	0.3
CdGa ₂ S ₄	2.2	0.5	0.35	2.0	0.45	0.35

[1] V. Yu. Rud', Yu. V. Rud', M.C. Ohmer, P.G. Schunemann. Semiconductors, **33**, 1317 (1999).

[2] Yu. V. Rud', I. A. Mal'tseva. Semiconductors,, **19**, 870 (1977).

[3] V. L. Panutin, B. E. Ponedel'nikov, A.E. Rozenson, B.H. Chijikov. Phisika. Izvestia Vuzov, 8, 57 (1979).

9. Current technical status

- on schedule, behind, ahead

All works are on schedule.

- refining next year schedule if necessary

- recommendation for changes of the work plan, if necessary

10. Cooperation with foreign collaborators

- exchange of scientific material (information, computer codes and data, samples)

We present Annual Reports, for 1 year (1 September 2001– 30 August 2002).

- signature of protocols (with short description)
- research carried out jointly

11. Problems encountered and suggestions to remedy

No

12. Perspectives of future developments of the research/technology developed

Attachment 1: Illustrations attached to the main text

Attachment 2: Other Information, supplements to the main text

Attachment 3: Abstracts of papers and reports published during the year of reference

Attachment 4: Information on patents and property rights.

III. ATTACHMENTS

I. Summary of personnel commitments for the year

Category I – 186 days and Category II – 185 days.

II. Equipment acquired during the year.

We have purchased new equipment – a photomultiplier with InP/InGaAs photocathode (Hamamatsu R5509-72).

Task 4 (part 1)

Photoconductivity of CdGa_2S_4 compounds were investigated starting from 1975 [1] and up to now not in detail [2-4] and only for nonpolarized light. As for HgGa_2S_4 there is no publications on this subject. Information about photoactive absorption on HgGa_2S_4 can be found only in one publication in which the results of the fabrication of photosensitive structures as well as the spectra of quantum efficiency of photoconversion η were presented [5]. In this publication also was used nonpolarized light, therefore the polarization dependences were not considered. It is evident that such studies with the linearly polarized light can be interesting for clarification the nature of optoelectronic phenomena in such a highly anisotropic CdGa_2S_4 and HgGa_2S_4 single crystals.

Photoconductivity spectra were detected by using grating monochromator SPM – 2. The spectral sensitivities of the monochromator and photomultiplier were corrected by the tungsten spectral lamp. The spectra were measured at the constant and modulated excitations when the photoconductivity signal was proportional to the intensity of the incident light. They were corrected by the equal number of incident photons. Spectral resolution was better than 1 meV. All measurements were performed at the room temperature due to the long time relaxations detected with the reducing temperature down to 77 K.

Measurements of the photoconductivity spectra were conducted with shining along the normal to (100) and (001) faces of the CdGa_2S_4 and HgGa_2S_4 crystals, that allowed to measure the coefficient of the photopolarization P_N [6], according to equation

$$P_N = (I^{\parallel} - I^{\perp}) / (I^{\parallel} + I^{\perp}) . \quad (1)$$

Here I^{\parallel} and I^{\perp} are photocurrents for the incident polarization radiation $E \parallel c$ and $E \perp c$, respectively.

Main results of measured for the first time polarized photoconductivity spectra of CdGa_2S_4 and HgGa_2S_4 crystals can be formulated as following:

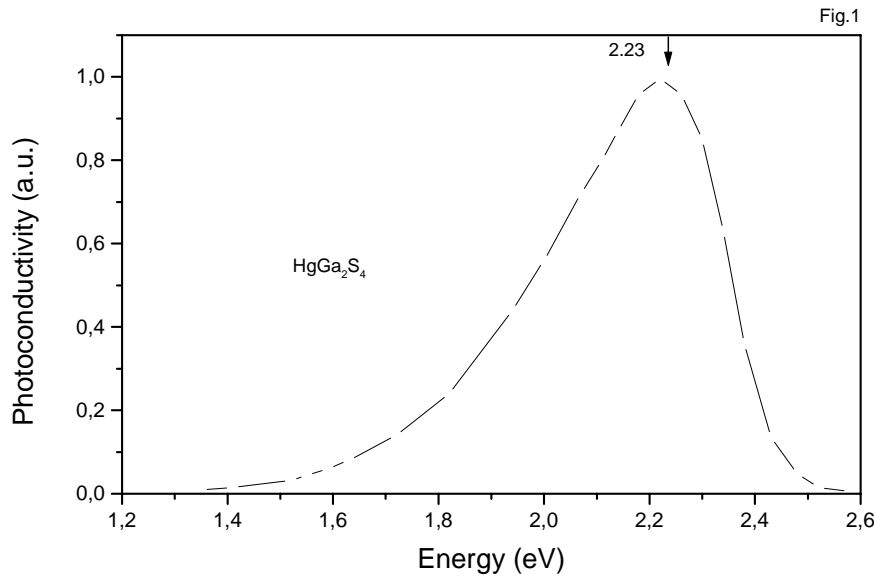


Fig.1. Spectral dependence of stationary photoconductivity of the HgGa_2S_4 single crystals (sample No. 7) at $T=300$ K for the nonpolarized excitation. Spectral resolution is better than 1 meV.

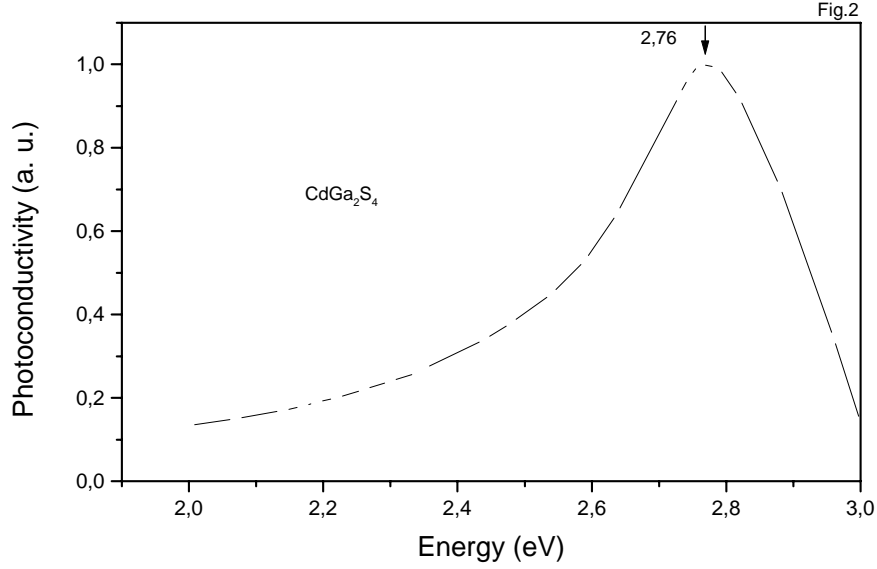


Fig. 2. Spectral dependence of stationary photoconductivity of the CdGa_2S_4 single crystals (sample No. 3) at $T=300$ K for the nonpolarized excitation. Spectral resolution is better than 1 meV.

- Figure 1 and 2 show typical of stationary photoconductivity of the HgGa_2S_4 CdGa_2S_4 single crystals respectively at $T = 300$ K. The photoconductivity spectra I^{\parallel} and I^{\perp} have maximum at $\hbar\omega^m = 2.23$ eV for HgGa_2S_4 and $\hbar\omega^m = 2.76$ for CdGa_2S_4 which are essentially less than the band gap of these semiconductors [7]. Therefore, the observed spectra can be attributed to the photoactive absorption with participation of lattice defects, located at the activation energies $E_D \approx 0.6$ eV (for HgGa_2S_4) and ≈ 0.8 eV (for CdGa_2S_4). The photoconductive bands in these crystals can be characterized also by full width at the half maximum $\delta \approx 0.38$ eV (for CdGa_2S_4) and $\delta \approx 0.4$ eV (for HgGa_2S_4). Large values of δ as well as the bands asymmetry with long-wavelength tailing indicate on nonelementarily and, therefore, on the complex energetic spectra of the lattice defects of the crystals under the study.
- Polarized photosensitivity for the both crystals for the case of registration the radiation along the normal parallel to the (100) is characterized by $I^{\parallel} > I^{\perp}$, while the azimuthal dependencies of the photocurrents follow to the periodical law

$$I_{\varphi} = I^{\parallel} \cos^2 \varphi + I^{\perp} \sin^2 \varphi, \quad (2)$$

where I^{\parallel} and I^{\perp} - are photocurrents for $\mathbf{E}_{rad} \parallel \mathbf{c}$ and $\mathbf{E}_{rad} \perp \mathbf{c}$, and φ is the azimuthal angle between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal \mathbf{c} . If we turn now to the photoresponse from the (001) plates it does not changes with the azimuthal angle and azimuthal dependence turns to the direct line. These results indicate that in these group of the crystals with defect chalcopyrite structure exist phenomenon of native photopleochroism and azimuthal dependencies of photoconductivity are in agreement with the crystalline symmetry of these compounds.

3. Spectra of the polarized photoconductivity for the HgGa_2S_4 for the both cases of the incident radiation polarizations have the same spectral shape (Fig. 3)

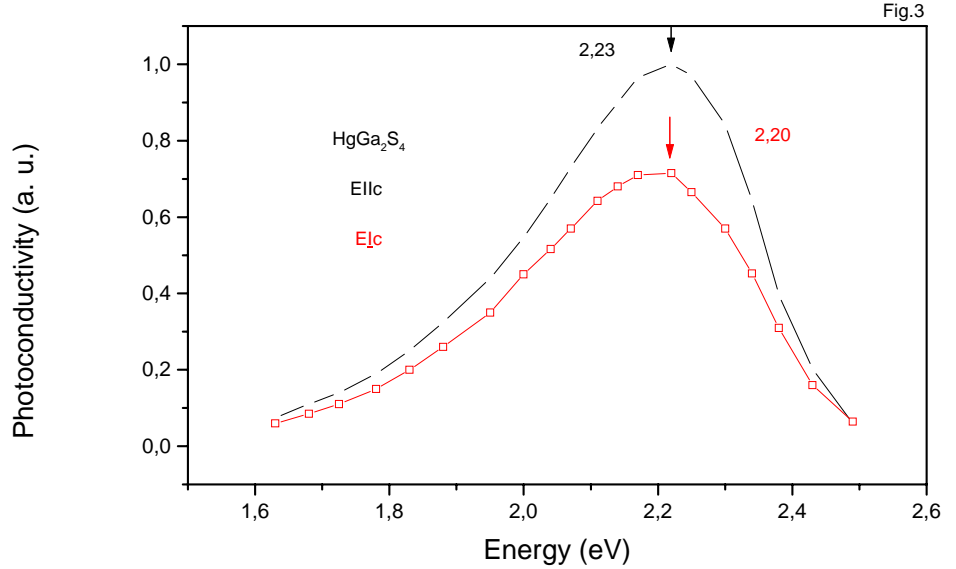


Fig. 3. Spectral dependencies of the stationary photoconductivity of the HgGa_2S_4 single crystals (sample No. 5, orientation of the plate – (100)) at $T=300$ K (the incident radiation polarizations are $E \parallel c$ and $E \perp c$).

The main observed features can be formulated as following: The maximums of the photoconductivity bands for the both polarizations are realized at the approximately equal values of the incident photon energy and, therefore, the polarization splitting of the impurity band does not appear. Thus, the polarization of radiation control mainly the value of the photoconductivity in the way that in the range of long-wavelength shoulder for the maximum of photoconductivity inequality $I^{\parallel} > I^{\perp}$ is satisfied. In the range of long-wavelength shoulder for the maximum of photoconductivity appears shoulder at $\hbar\omega = 2.37$ eV for $E \perp c$. This leads to the positive sign of the maximum polarization difference of photoconductivity $\Delta = I^{\parallel} - I^{\perp}$ and its maximum is localized in the range of the photoconductivity maximum. The sign of the polarization difference of maximum photoconductivity allows to look for selection rules of optical transitions, responsible to the maximum photoconductivity of the HgGa_2S_4 single crystals.

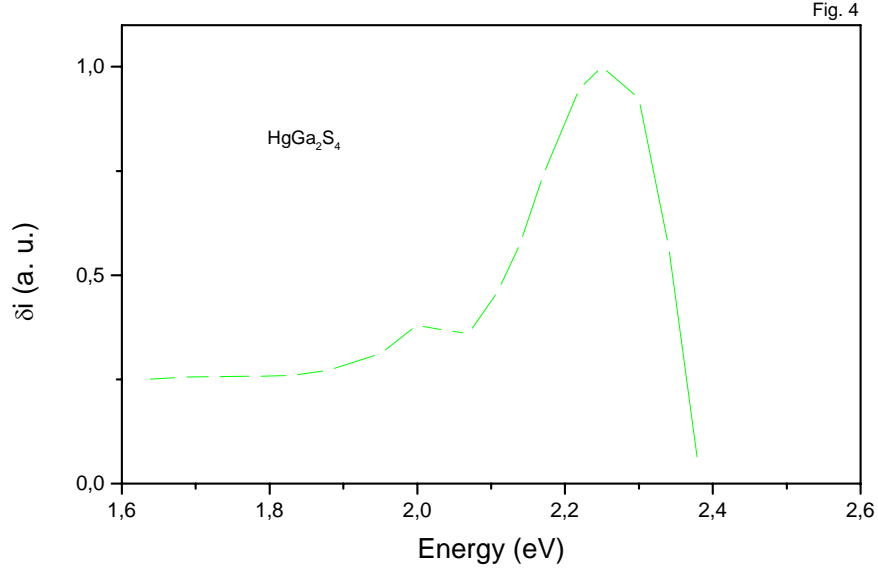


Fig. 4. Spectral dependencies of the polarization difference of photoconductivity of the HgGa_2S_4 single crystals (sample No. 5, orientation of the plate – (100)) at $T=300$ K.

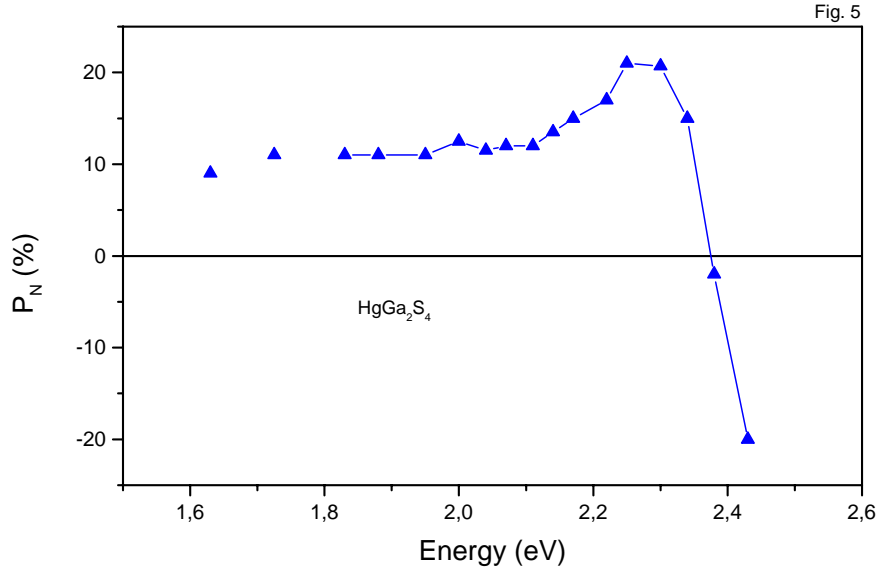


Fig. 5. Spectral dependencies of the coefficient of native photopletochroism of the HgGa_2S_4 single crystals (sample No. 5, orientation of the plate – (100)) at $T=300$ K.

Finally, in accordance with the sign of Δ the coefficient of native photopletochroism of the HgGa_2S_4 single crystals, as is evident from the Fig. 5, also has positive sign in the range of the long-wavelength maximum of photoconductivity. The maximum

value $P_N \approx 20\%$ is achieved near the $\hbar\omega = 2.37$ eV. It is important to note that there is also a strict decrease of the amplitude of P_N and an inversion of its sign in the range of the strict cut-off of the photoconductivity. The reason of such inversion can be connected as with the increase of the surface recombination velocity as well as with changing the selection rules with the changing of the incident photon energy in the range of strong interband absorption. For final selection between these possibilities it is needed further study of interconnections of the polarization photoconductivity measurements and technological aspects of the growth processes of these ternary compounds.

- Fig. 6 shows typical dependencies of the stationary photoconductivity of the (100) plate of the CdGa_2S_4 single crystals at $T = 300$ K for polarized light

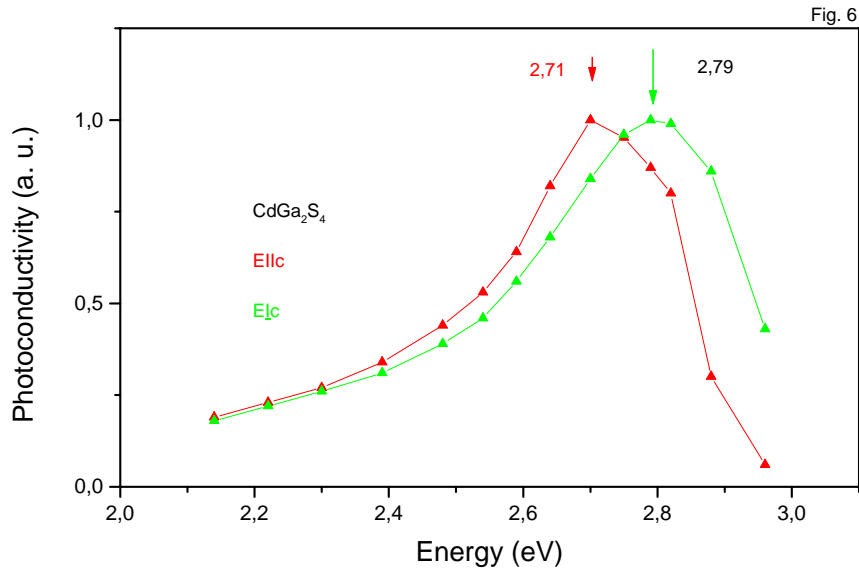


Fig. 6. Spectral dependencies of the stationary photoconductivity of the CdGa_2S_4 single crystals (sample No. 3, orientation of the plate – (100)) at $T=300$ K (the incident radiation polarizations are $E_{||c}$ and $E_{\perp c}$).

In principle, observed dependencies and features of polarization photoconductivity in this material are close to that observed for HgGa_2S_4 . At the same time, for linear excitation polarization for CdGa_2S_4 we have found more pronounced polarization splitting of photoconductivity spectra $\Delta\hbar\omega = 0.1$ eV. In particular this can be the consequence of the high tetragonal deformation of crystalline lattices of the CdGa_2S_4 with respect to that of the HgGa_2S_4 . As a result, at $\hbar\omega < 2.75$ eV the photoconductivity obey the inequality of $I^{||} > I^{\perp}$ as for the HgGa_2S_4 while at $\hbar\omega > 2.75$ eV these inequality transforms to the form of $I^{||} < I^{\perp}$. As a result in the spectra of the polarization difference of photoconductivity (Fig. 7) and the coefficient of the photopoleochroism P_N of the CdGa_2S_4 single crystals

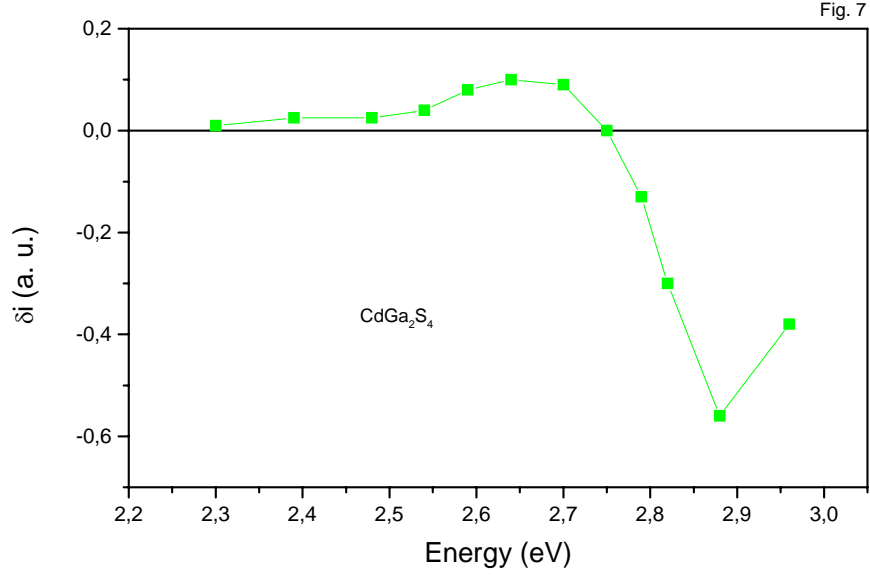


Fig. 7. Spectral dependencies of the polarization difference of photoconductivity of the CdGa_2S_4 single crystals (sample No. 3, orientation of the plate – (100)) at $T=300$ K.

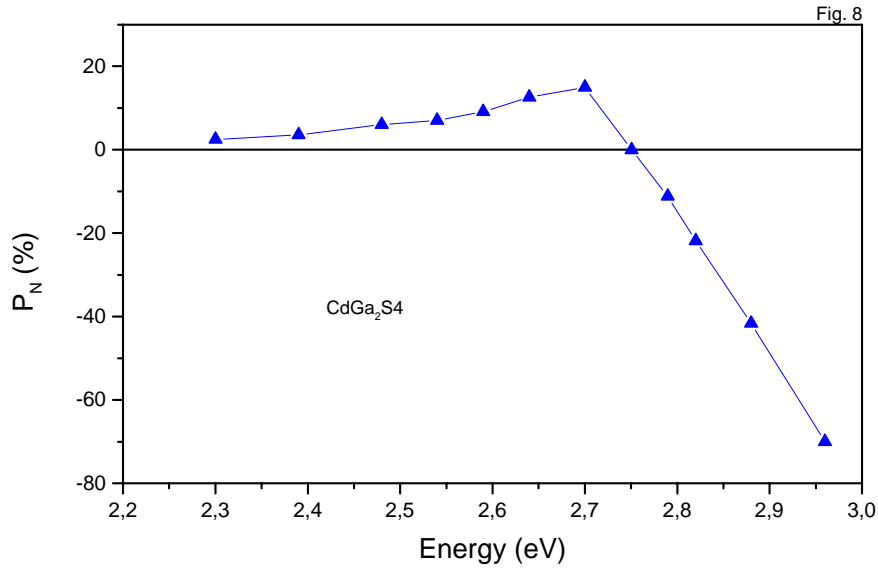


Fig. 8. Spectral dependencies of the coefficient of native photopoleochroism of the CdGa_2S_4 single crystals (sample No. 5, orientation of the plate – (100)) at $T=300$ K.

appeared nontypical for the isotropic media the photoisotropic point at which $\Delta=0$, and correspondingly $P_N=0$.

As in the case of the HgGa_2S_4 crystals, the reason of the observed inversion of The sign of the native photopoleochroism from the positive to the negative in the range of short-wavelength cut-off of the photoconductivity can be connected as with the increase of the surface recombination velocity of

photogenerated pairs as well as with the appearance of optical transitions with other selection rules changing the selections rules. This question requires further special study.

5. So, polarization dependent measurements of the photoconductivity spectra on the CdGa₂S₄ and HgGa₂S₄ crystals, for the first time, allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The observed dependencies are rather complicated and may depend on the nature of the lattice defects and also on presence of close lying energies of the optical transitions that have different selections rules.

Referencies

1. S.I. Radauzan, V.Ph. Jitar', V.S. Donu. Semiconductors, **9**, 1018 (1975).
2. P. Kivits, M. Wijnakker, J. Claassen. J.Phys.C: Sol. St. Phys., **11**, 2361(1978).
3. A.N. Georgobiani, S.I. Radautsan, I.M. Tiginyanu. Phys. St. Sol. (a), **69**, 513(1982).
4. A.N. Georgobiani, A.N. Gruzintsev, I.M. Tiginyanu. Short Report on Physics. N 2, 3(1981).
5. V.Yu. Rud', Yu.V. Rud', M.C. Ohmer, P.G. Schunemann. Semiconductors. **33**, 1108 (1999).
6. [4] F. P. Kesamanly, Yu.V. Rud', Semiconductors. 30, 346, (1996).
7. Fiziko-khimicheskie svoistva poluorovodnikovyx veshestv Moscow, Nauka, 1979.

Task 4 (part 2)

Our measurements of the photoconductivity spectra of CdGa₂S₄ and HgGa₂S₄ compounds oriented in the (100) plane show that native photopleochroism coefficient in these crystals has additional sign in the range of the maximum of the photoconductivity and the maximum value of P_N≈20% for HgGa₂S₄ crystals and P_N≈10% for CdGa₂S₄.

This anisotropy of the photoconductivity revealed in the range of impurity absorption by the lattice defects. We study the characteristic of local distribution of the experimental polarized indicatris of the potoconductivity by varying the exciting light position along the (100) plane.

It was essential to obtain information about the homogeneity of the samples studied. Therefore in contrast to our earlier measurements we have used focused linearly polarized beam. The diameter of the focus was in the range 0.2-0.3 mm.

We measured the polarized dependencies of the photoconductivity i_{φ} on the azimuthal angle φ between the polarization of the electric field vector \mathbf{E}_{rad} and tetragonal axis of the crystal c .

Figure 1 shows typical examples of the azimuthal dependencies of photoconductivity i_{φ} of the for one of the CdGa₂S₄ single crystal sample under the fixed photon energy excitation $\hbar\omega_{exc}$, that corresponds to the maximum value of native photopleochroism coefficient P_N.

With shifting the position of 0.2 mm light beam exciting the photoconductivity we have found that experimental curves obey to the theoretical dependencies

$$I_{\varphi} = I^{\parallel} \cos^2 \varphi + I^{\perp} \sin^2 \varphi, \quad (2)$$

where I^{\parallel} and I^{\perp} - are photocurrents for $\mathbf{E}_{rad} \parallel \mathbf{c}$ and $\mathbf{E}_{rad} \perp \mathbf{c}$. For the 5x5 mm² photoaccepting plane usually about 30 photoconductivity excitation points were measured.

It was found that the positions of the photoconductivity maximum always corresponds to the $\mathbf{E}_{rad} \parallel \mathbf{c}$, while photoconductivity minimum always observed for the $\mathbf{E}_{rad} \perp \mathbf{c}$ case.

This means that all ranges of the surfaces studied are similar. In such a case the observed spread of the measured values for the photoconductivity ratio in each of n-zone, where n is the natural sequence of numerical numbers, corresponding to the number of the excitation, $\Delta_n = i_n^{\parallel} / i_n^{\perp}$ can be related to positional ordering in the range of n-zone.

The measured Δ_n values for the CdGa₂S₄ single crystal sample show the spread of the photoconductivity ratio in the range 1.25 – 1.45. This spread matches to the native photopleochroism coefficient P_N in the range 11 –18% at T + 300 K.

Figure 2 shows typical examples of the azimuthal dependencies of photoconductivity i_{φ} of the for one of the HgGa₂S₄ single crystal sample that also has the (100) orientation for photoacceptance plane.

Curves 1 and 2, as in the case of CdGa₂S₄ single crystals, cover the whole range of the Δ_n from the minimal up to the maximal for the all samples used.

Typical average photoacceptance square was 3x3 mm² when we able to measure up to 20 photoconductivity excitation zones.

The main result of our analyses of the changes of local distribution of the polarized indicatris of the potoconductivity i_{φ} and ratio Δ_n by scanning the exciting light position along the (100) plane is that the all angels at which maximum values of the photoconductivity is observed corresponds to the polarization the $\mathbf{E}_{rad} \parallel \mathbf{c}$, while potoconductivity minimum observed only for the $\mathbf{E}_{rad} \perp \mathbf{c}$ case.

The spread of the photoconductivity ratio for the HgGa₂S₄ single crystals is in the range 1.4 – 1.7 that means that the native photopleochroism coefficient P_N for the HgGa₂S₄ single crystals reaches the range 17 –25% at T + 300 K.

In summary, our study of the azimuthal dependencies of photoconductivity i_{φ} of the CdGa₂S₄ and HgGa₂S₄ single crystals allow to establish that the positive the native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane. The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axisies [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the HgGa₂S₄ CdGa₂S₄ single crystals.

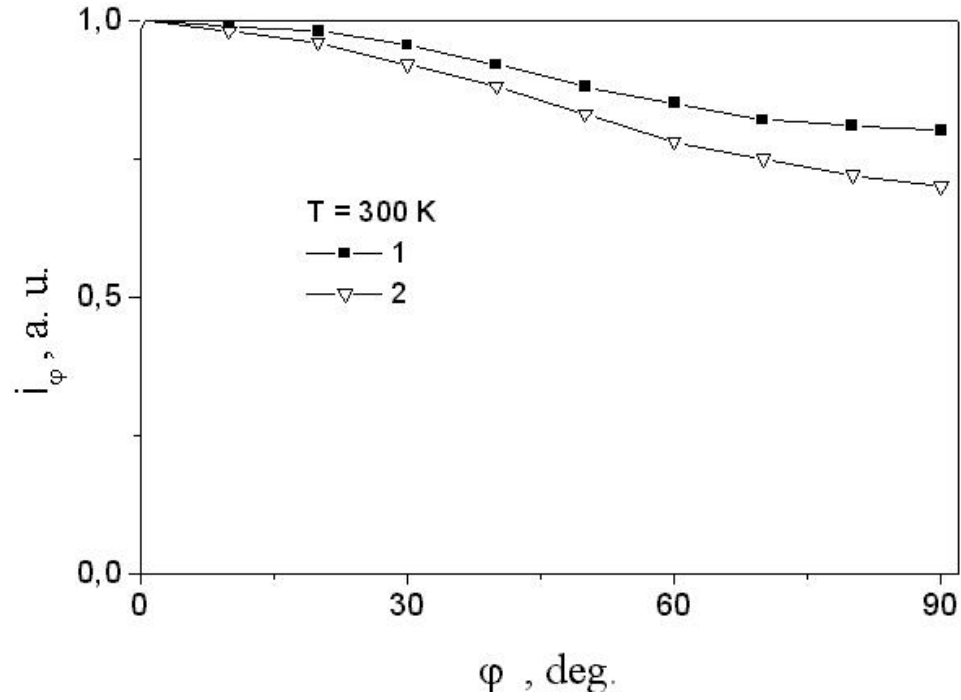


Fig. 1. Azimutal dependence of stationary photoconductivity i_φ of the CdGa_2S_4 single crystals at $T=300$ K (Sample No. 5, curve 1 – excitation range of the photoconductivity with the minimal value of the polarization ratio $\Delta_n \approx 1.25$, curve 2 – excitation range with the maximal value of the polarization ratio $\Delta_n \approx 1.43$, the excitation photon energy $\hbar\omega_{\text{exc}} = 2.7$ eV, solid curves are the theoretical dependencies according to the Eq. 1, points are experimental data).

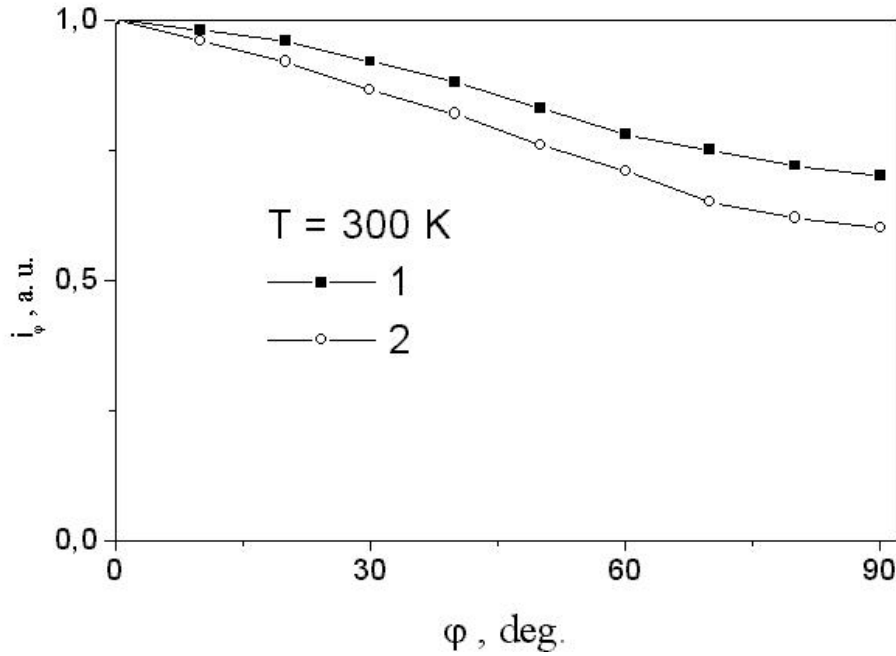


Fig. 2. Azimuthal dependence of stationary photoconductivity i_ϕ of the HgGa_2S_4 single crystals at $T=300$ K (Sample No. 11, curve 1 – excitation range of the photoconductivity with the minimal value of the polarization ratio $\Delta_n \approx 1.41$, curve 2 – excitation range with the maximal value of the polarization ratio $\Delta_n \approx 1.67$, the excitation photon energy $\hbar\omega_{\text{exc}} = 2.7$ eV, solid curves are the theoretical dependencies according to the Eq. 1, points are experimental data.

Task 4 (part 3)

Our experimental search performed allowed to find lowohmic nonrectified contacts that together with the high resistance of the CdGa_2S_4 and HgGa_2S_4 compounds permitted to conduct measurements of the photoconductivity spectra of the both compounds. As a result we were able to detect the photoconductivity spectra of the HgGa_2S_4 down to $T = 77$ K and for the CdGa_2S_4 down to $T = 150$ K.

The main results are following:

Figure 1 and 2 show typical spectral dependencies of the stationary photoconductivity i_ϕ of the for electrically homogeneous CdGa_2S_4 and HgGa_2S_4 single crystals. For the both cassis $i_\phi \sim L$, the density of incident polarized excitation. This situation vase the base for normalizing the photoconductivity signal to the equal number of the incident photons. We note that the surface mapping measurements with the diameter of the laser focus of 0.2 mm did not show any photovoltage that additionally indicate sufficiently high homogeneity of the samples measured. We note also that the spectra presented in Figs. 1

and 2 are well reproduced that also indicate that there are no “frozen” photoconductivity in our samples.

2. The spectra of the stationary of photoconductivity presented in Figs. 1 for the n-HgGa₂S₄ show broad structureless features (curves 1 and 2). Full widths at the half maximum (FWHM) $\delta_{1/2} \approx 400$ meV and practically independent on the temperature in the range 77-300 K as well as on orientation of the polarization of the electric field vector E_{rad} along the tetragonal axis of the crystal c . With reduction temperature down to 80 K, as a rule, the photoconductivity 2-2.5 times increased with the shift of the maximum energy position to the short wavelength with a linear law with a speed of $\beta \approx -5 \cdot 10^{-4}$ eV/K. This value is close to the temperature coefficient of the band gap E_G for the diamond like crystals [1]. The absolute maximum of the photoconductivity of the HgGa₂S₄ single crystals are realized at the energies sufficiently lower the band gap of the HgGa₂S₄. Therefore, the observed photoconductivity should be connected to the photoactive absorption from deep levels of lattice defects and possibly also to “pseudodirect” interband transitions [2]. Appearance of the sharp longwavelength maximum at LNT (Fig. 1 curve 4) indicate on the increase of the role of the deep centers located at ~ 1.1 eV from one of the free zones.

From the Fig. 1 it also is evident that the observed photoconductivity at $T = 300$ K in the excitation photon energy range $\hbar\omega_{exc} < 2.38$ eV is dominated for the $E_{rad} \parallel c$ polarization, while for the energies higher then this value the influence of the polarization of the incident excitation is changed to the opposite. The existence of the photoisotropic point $\hbar\omega_1$ in the spectra of the HgGa₂S₄ single crystals can be related to the change of the selection rules for the corresponding optical transitions or due to the increased influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. The latter become active with the shift of the absorption zone at near the surface range, as it was observe early in the case of the III-V compounds [3].

The spectral dependence of the native photopleochroism coefficient P_N for the typical the HgGa₂S₄ crystals is given in the Fig. 3. It seen that in the longwavelength range on the relatively weak optical absorption edge the sign of the native photopleochroism coefficient is positive and its maximum value is sufficiently low relatively to the characteristic one for the ternary II-IV-V₂ compounds [4] and does not exceed 10 – 15%. Huge increase of the amplitude of the native photopleochroism coefficient is detected in the spectral range of the grows of the optical absorption. This observation gives the base to connect the increase of the negative native photopleochroism coefficient to the high velocity of the surface recombination. Really, this process of the surface recombination should be first of all reflected on the strongly absorbed $E_{rad} \parallel c$ excitation and as a result the excitation with $E_{rad} \parallel c$ gives $i^\perp > i^\parallel$ (Fig. 3).

The fact that the spectral dependencies of the native photopleochroism coefficient features do not exhibit any changes during varying the temperature in the range 77 – 300K also indicate that there are not observed any structural phase changes in this temperature range.

3. From Fig. 3 it is become evident that upon changing the Hg atoms to Cd practically all the above-considered features for the HgGa₂S₄ single crystals are reproduced in the case of the CdGa₂S₄ single crystal. At the same time in the longwavelength range of the stationary of photoconductivity spectra $i^\perp > i^\parallel$, and at the transition from the firstly observed by us photoisotropic point ($i^\perp > i^\parallel$) this inequality is inverted into $i^\perp < i^\parallel$ (Fig.

2). The quantity differences are due to the strong shift to the longwavelength range of the photoisotropic point in the CdGa_2S_4 crystals with respect to the HgGa_2S_4 crystals. The position of the photoisotropic point is intermediate between the energy of the maximums of the photoconductivity for the polarizations $\mathbf{E}_{\text{rad}} \parallel \mathbf{c}$, and $\mathbf{E}_{\text{rad}} \perp \mathbf{c}$.

We find that in the CdGa_2S_4 crystals the native photopleochroism coefficient and its temperature dependence given in the Fig. 4 are also similar to the above-considered case of the HgGa_2S_4 crystals.

4. The analysis of the observed results allows to formulate that for the clarification of the reasons that cause inversion of the sign the native photopleochroism coefficient in the CdGa_2S_4 and HgGa_2S_4 compounds it is need first of all to suppress the influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. It is evident, that the one of the most effective ways to solve this problem may be creation of the photosensitive structures the CdGa_2S_4 and HgGa_2S_4 compounds.

References

- [1] Physical and Chemical properties of semiconductors. Moscow, Nauka, 1979.
- [2]. J.L. Shay, J.H. Wernick. *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications*. (Oxford, Pergamon Press, 1975).
- [3] A A Abdurachmanov, and Yu V Rud', Semiconductors, 16, 959 (1982).
- [4] F P Kesamanly, and Yu V Rud', Semiconductors, 33, 513 (1998).

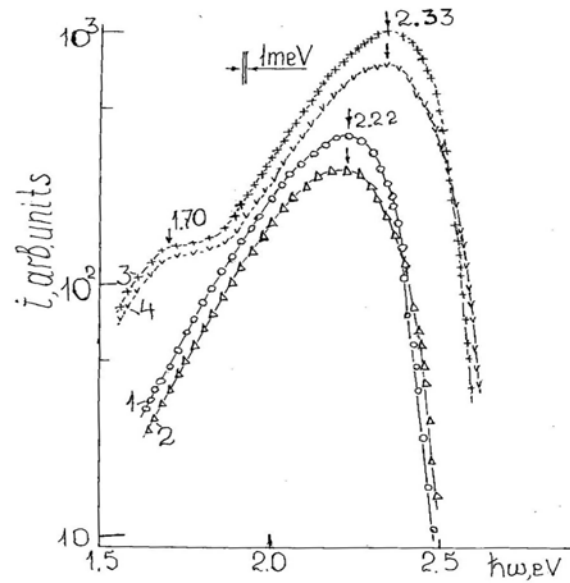


Fig. 1. Spectral dependencies of the stationary photoconductivity of the HgGa_2S_4 single crystals in the linearly polarized excitation; Sample No. 7; T,K: 300 – curves 1 and 2, 80 – curves 2 and 4; The incident radiation polarizations are $\mathbf{E} \parallel \mathbf{c}$ – curves 1 and 3, and $\mathbf{E} \perp \mathbf{c}$ – curves 2 and 4). Orientation of the excitation crystallographic face is (100). The incident angle $\Theta=0^\circ$.

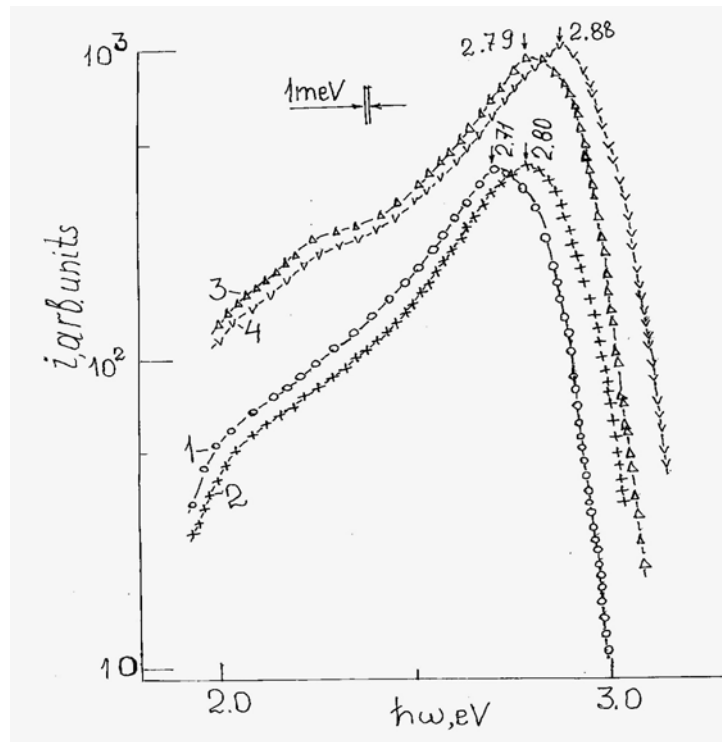


Fig. 2. Spectral dependencies of the stationary photoconductivity of the CdGa_2S_4 single crystals in the linearly polarized excitation; Sample No. 11; T, K: 300 – curves 1 and 2, 150 – curves 3 and 4; The incident radiation polarizations are $\mathbf{E} \parallel \mathbf{c}$ – curves 1 and 3, and $\mathbf{E} \perp \mathbf{c}$ – curves 2 and 4). Orientation of the excitation crystallographic face is (100). The incident angle $\Theta=0^\circ$.

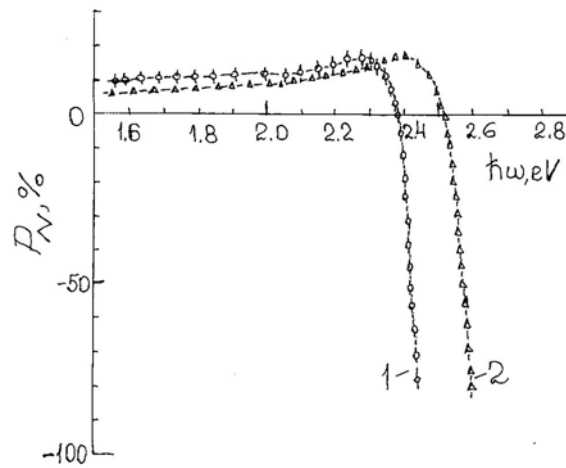


Fig. 3. Spectral dependencies of the native photopoleochroism coefficient in the HgGa_2S_4 compounds; Sample No. 7; T, K: 300 – curve 1, 80 – curves 2. The incident angle $\Theta=0^\circ$.

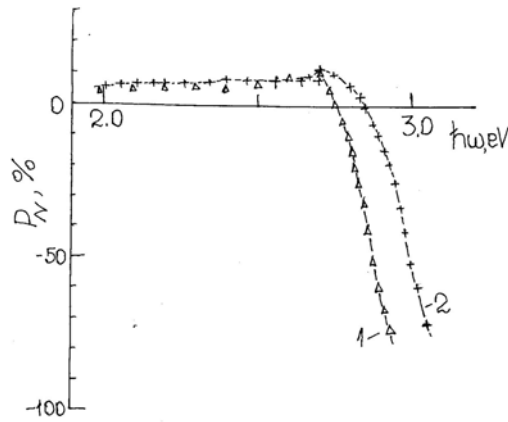


Fig. 4. Spectral dependencies of the native photopleochroism coefficient in the CdGa_2S_4 compounds; Sample No. 11; T, K: 300 – curve 1, 150 – curves 2. The incident angle $\Theta=0^\circ$.

Table 1.

Physical properties of the HgGa_2S_4 and CdGa_2S_4 single crystals

Compound	Space group	Lattice parameters, Å		τ c	E_g , eV
		a		%	
HgGa_2S_4	S_4^2	5.50	10.23	14	2.8
CdGa_2S_4	S_4^2	5.577	10.08	19	3.58

Table 2.

Photoluminescence parameters of the HgGa_2S_4 and CdGa_2S_4 single crystals

Compound	300 K			77 K		
	$h\nu^m$, eV	δ_s , eV	P, %	$h\nu^m$, eV	δ_s , eV	P, %
HgGa_2S_4	2.0	0.45	30	1.8	0.4	30
CdGa_2S_4	2.2	0.5	35	2.0	0.45	35

Task 5

Our experimental search was devoted toward study of electrical properties and optical absorption of the HgGa_2S_4 single crystals, study of contact properties of these crystals with some metals with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion.

The main results are following:

1. We have used the HgGa_2S_4 single crystals grown in the ultralow temperature gradient by horizontal crystallization from the melts close to the stehiometric [1]. Typical dimensions of the samples used for the measurements of kinetic coefficients were $0.6 \times 0.9 \times 4.5 \text{ mm}^3$. All these samples showed n-type conductivity determined by the sign of thermoelectric power, while the samples with p-type were not obtained. Our measurements of the Hall constant on the homogeneous samples show that

concentration of the free electrons is rather small ($n \approx 10^8 - 10^9 \text{ cm}^{-3}$) and the specific electrical resistance $\rho \approx 10^9 - 10^{10} \text{ Ohm}\cdot\text{cm}$.

Figure 1 show typical temperature dependence of the specific electrical resistance in the temperature range $T = 77 - 300 \text{ K}$. It is seen that exponential falling of the resistance with increasing temperature at $T > 77 \text{ K}$. Note that activation energy for the donors, keeping in mind strong compensation of the acceptors, is rather small $E_D \approx 37-40 \text{ meV}$. So we establish for the first time for the HgGa_2S_4 single crystals grown in the ultralow temperature gradient by horizontal crystallization from the melts close to the stehiometric that shallow level donors are created. Early, this fact was not known for this group of semiconductors.

2. We establish that mechanical contact of pure metal layers of (In [2], Ni, Au, Ag) with the cleaved surface of the HgGa_2S_4 single crystals and further with chemically polished surface of electrically homogeneous HgGa_2S_4 give rectifying characteristics. Fig. 2 shows typical stationary current-voltage characteristics for the one of the best surface-barrier In- π - HgGa_2S_4 structures (curves 1 and 1'). Rectification determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 20 \text{ V}$, reaches the values $K \approx 200$, that is the record value obtained up to now for the the n - HgGa_2S_4 single crystals. Initial part of the current-voltage direct line (Fig. 1, curve 1) follows to the diode equation for the bias range $U < 5 \text{ V}$ with diode strength $n \approx 10$, while with the illumination (Fig. 2, curve 2) this value falls up to the $n \approx 2$. The high values of n , reflect the influence of high simultaneous resistance that does not allow to find mechanisms of direct current flow. In the bias range $U > 10 \text{ V}$ the current-voltage characteristics follow to the linear law

$$I_{\text{dir}} = (U - U_0) / R_0, \quad (1)$$

Where the residual resistance without illumination of the structure $R_0 \approx (2-2.5) \cdot 10^7 \Omega$ falls up to $R_0 \approx (6-8) \cdot 10^5 \Omega$. We see from Fig. 2 that direct and reverse current-voltage characteristics in the case of illumination (curves 2 and 2') shifts relatively darks in the direction of increasing direct and reverse currents. Observed reducing of the diode diode strength n of the illuminated structures at the first is induced by significant fall of R_0 under the illumination. The reverse current for In- π - HgGa_2S_4 barriers usually is in the range $I_{\text{rev}} \approx 10^{-9} \text{ A}$ and increases with increasing the bias by a low $I_{\text{rev}} \sim U_{\text{rev}}^\gamma$, where $\gamma \approx 1.08$. This value indicate nonperfect periphery of the first obtained structures. The latter is limited by the limited size of available crystals and indicate the real way of further improvement of the surface-barrier structure characteristics on the base of HgGa_2S_4 with solving size and crystal perfection problems.

Under illumination of the surface-barrier structures on the base of n - HgGa_2S_4 photovoltaic effect was also observed. Photovoltage of the free motion in the surface-barrier structures on the base of n - HgGa_2S_4 single crystals is dominated under conditions of illumination of the structures from the side of barrier contacts. In this case the sign of the photovoltage always corresponds to the direction of the rectification in the structures and independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. These established facts on the structures obtained for the first time can be used as a base to connect rectification and photovoltaic effect with energy barrier at the contact of semiconductor with metal studied. Maximum value of the

voltage photosensitivity achieved for the surface-barrier In-*n*-HgGa₂S₄ structures is $2 \cdot 10^3$ V/W at $T=300$ K.

3. Typical spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier In-*n*-HgGa₂S₄ structures are given in the Fig. 3. It is seen that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 0.8-3.8 eV (Fig. 3, curve 1). The spectral parameter η at $\hbar\omega < 2.2$ eV strongly changes from structure to structure, that may be due to the differences of the crystal properties and, therefore, may be used for the diagnostic of the material perfection. Under). Under condition of illumination of firstly obtained structures from the substrate side at the photon energy range $\hbar\omega > 2.25$ eV in the η spectra appears sharp cut-off of the photosensitivity (Fig. 3, curve 2). This cut-off may indicate on increase of the optical absorption in the HgGa₂S₄ plate. As a result of this process, the photogeneration area more and more moves from the active area and localizes at the thin surface layer of semiconductor. It can be supposed that due to small length of a diffusion shift of the nonequilibrium charge carriers the concentration of the photogenerated carriers, which achieve the active area, with increasing the photon energy $\hbar\omega > 2.3$ eV begin to fall and, therefore, the quantum efficiency of photoconversion $\eta \rightarrow 0$. It is important to note that the cut-off spectral range of η under the condition of illumination of Shottky barriers from the substrate side is in an agreement with a beginning of sharp increase of the optical absorption coefficient α (Fig. 4) exactly at photon energy $\hbar\omega \approx 2.3$ eV. This value can be used as a preliminary estimation of the absorption edge E_G of this little known semiconductor. The $\eta(\hbar\omega)$ spectra in the range of $\hbar\omega < 2.25$ eV are practically independent on illumination geometry of the surface-barrier structures (Fig.3, curves 1 and 2) that is due to the bulk nature of the charge carrier photogeneration in the HgGa₂S₄ crystals. The longwavelength edge of the photosensitivity of the surface-barrier structures in the range of $\hbar\omega < 2.2$ eV follows to the Fowler law and, therefore, is rectified in the coordinates $(\eta\hbar\omega)^{1/2} - \hbar\omega$ (Fig. 5). From the extrapolation of the direct linear parts $\eta^{1/2} \rightarrow 0$ we obtain first estimation of the energy height of In-*n*-HgGa₂S₄ and Ag-*n*-HgGa₂S₄ structures $\phi_D \approx 1.1$ eV at $T=300$ K. Note, that for some barriers in the dependencies $(\eta\hbar\omega)^{1/2} - \hbar\omega$ revealed several direct linear parts and , correspondingly, several cut-off energies (Fig. 5). This situation may reflect complicated nature of the energy band structure of the HgGa₂S₄ crystals.

The increase of the photoconductivity in the best surface-barrier structures at $\hbar\omega > 2.3$ eV under the condition of illumination of the structures from the barriers side (Fig. 3, curve 1) can be related with the fundamental absorption in the HgGa₂S₄ crystals, that is not possible to detect by traditional absorption spectroscopy techniques on such a small size samples (Fig. 4). From the Fig.6 it is seen that increase of the photoconductivity in the best surface-barrier structures at the photon energy range of 2.3-2.8 eV follows the $(\eta\hbar\omega)^{1/2} - \hbar\omega$ law (curve 1). Extrapolation of this dependence $(\eta\hbar\omega)^{1/2} \rightarrow 0$ allows to estimate the energy of indirect interband optical transitions $E_G^{in} \approx 2.27$ eV for *n*-HgGa₂S₄ at $T=300$ K. More sharp increase of the photoconductivity in the surface-barrier structures at the photon energy range of $\hbar\omega > 2.8$ eV follows to the characteristic for the direct optical transitions quadratic $(\eta\hbar\omega)^2 - \hbar\omega$ law (curve 2). Extrapolation of this dependence $(\eta\hbar\omega)^2 \rightarrow 0$ allows to estimate the energy of direct interband optical transitions $E_G^{dir} \approx 2.86$ eV for *n*-HgGa₂S₄ at $T=300$ K. This value is in a good agreement with results of Ref. [3].

4. So, in this work for the first time, the problem of creation of the photosensitive structure on the base of $n\text{-HgGa}_2\text{S}_4$ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of $n\text{-HgGa}_2\text{S}_4$ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

Referencies

- [1]. P.G. Schunemann, T.M. Pollak. MRS Bulletin. **23**, 23 (1998).
- [2]. V.Yu. Rud', Yu.V. Ru', M.C. Ohmer, P.G. Schunemann. Semiconductors, **33**, 1108 (1999).
- [3]. A.N. Georgobiani, S.I. Radautsan, I.M. Tiginyanu. Semiconductors, **19**, 193 (1985).

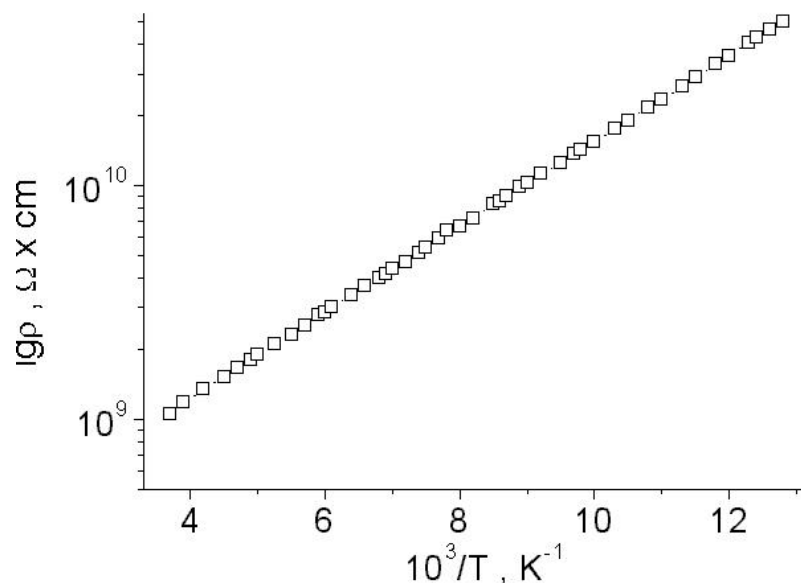


Fig. 1. Temperature dependencies of the specific resistance stationary photoconductivity of the HgGa_2S_4 single crystals; Sample No. 7n.

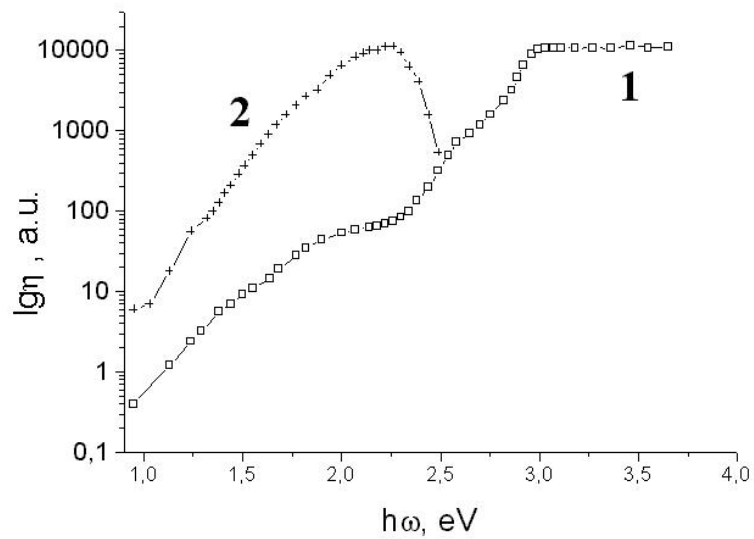


Fig. 2. Stationary (curves 1 and 1') and light (curves 2 and 2') current-voltage characteristics of In-*n*-HgGa₂S₄ at $T=300$ K (Sample 17n. Transmission direction is realized at the external positive bias at the barrier contact. Power density of illumination lamp $L \approx 1 \text{ mW/cm}^2$. Curves 1' and 2' are reverse branches of current-voltage characteristics).

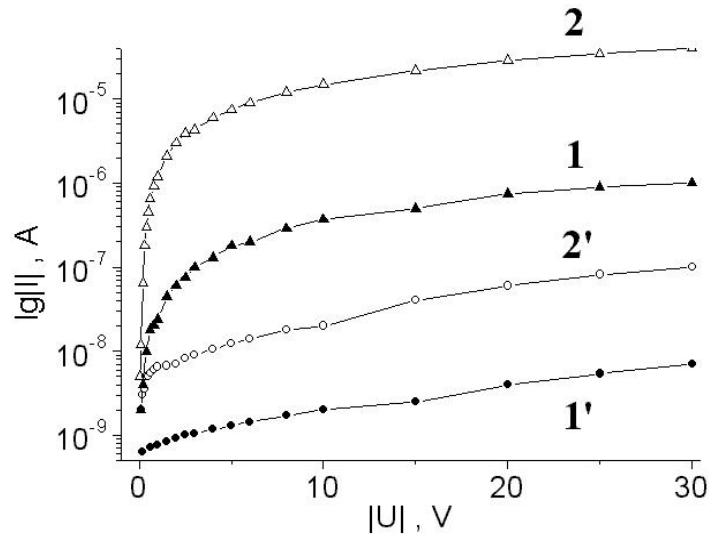


Fig. 3. Spectral dependencies of the relative quantum efficiency photoconversion of the surface-barrier In-*n*-HgGa₂S₄ structures in the coordinates $\eta^{1/2} - h\omega$ at $T=300$ K in the unpolarized radiation (Sample 17-3n). Illumination from the barrier contact side – curve 1 and from the substrate side – curve 2. Spectral resolution better than 1 meV.

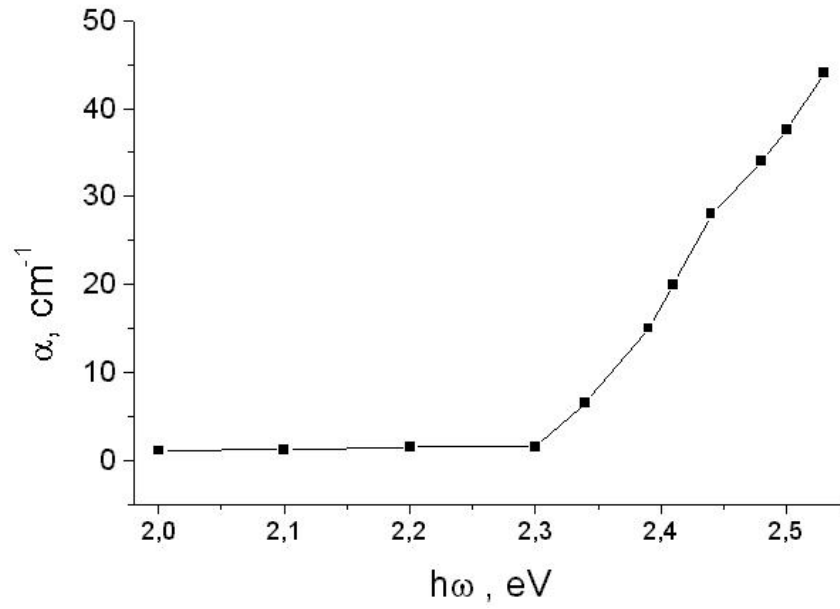


Fig. 4. Spectral dependencies of the optical absorption coefficient n -HgGa₂S₄ single crystal at $T=300$ K (Sample 17-3n. Sample size $0.6 \times 2.1 \times 4.3$ mm³).

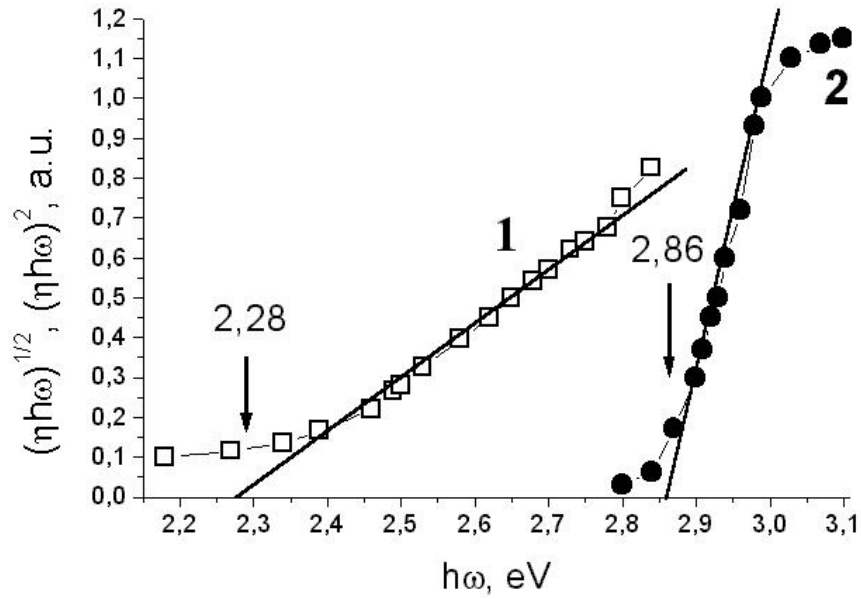


Fig. 5. Spectral dependencies of the relative quantum efficiency of the photoconversion for the surface-barrier In- n -HgGa₂S₄ structures in the coordinates $(\eta\hbar\omega)^{1/2} - \hbar\omega$ at $T=300$ K (Sample 15-n). Illumination of the structure by nonpolarized radiation from the energy barrier contact side. Arrows indicate the values of cut-off energy.

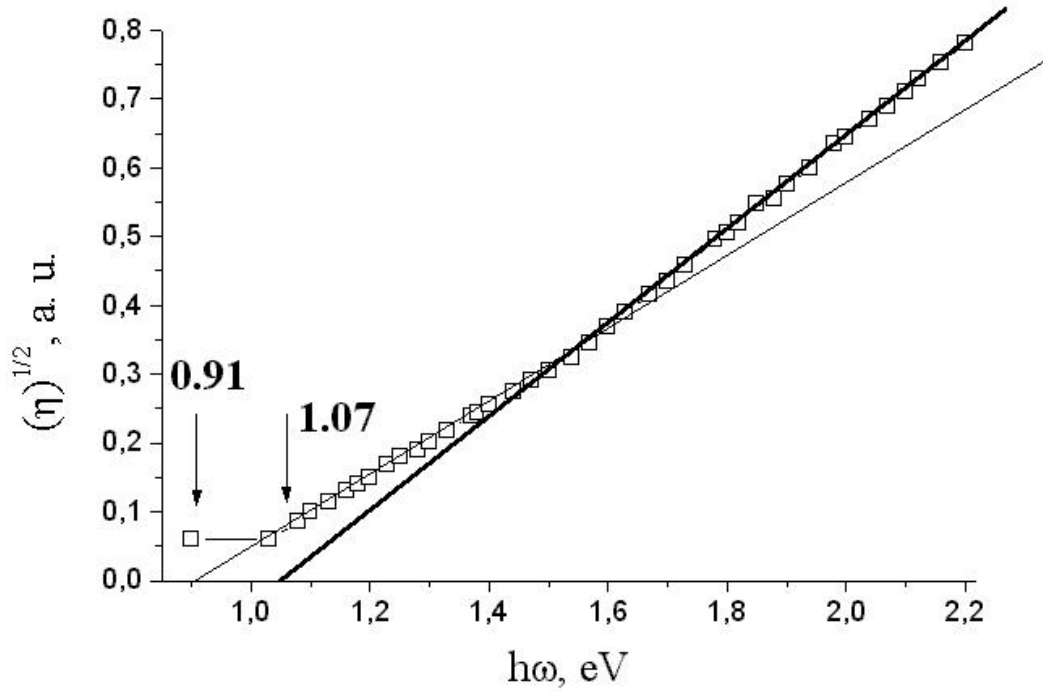


Fig. 6. Spectral dependencies of the relative quantum efficiency of the photoconversion for the surface-barrier In-*n*-HgGa₂S₄ structures in the coordinates $(\eta\hbar\omega)^{1/2} - \hbar\omega$ - curve 1 and $(\eta\hbar\omega)^{1/2} - \hbar\omega$ - curve 2 for the nonpolarized radiation at $T=300$ K. Illumination of the structure from the energy barrier contact side. Arrows at curves 1 and 2 indicate the values of cut-off energy.

- compliance with tasks and milestones as described in the work plan
All works are in compliance with tasks and milestones.
- achievements of the past year

Our polarization dependent measurements of the photoconductivity spectra on the CdGa₂S₄ and HgGa₂S₄ crystals, for the first time, allow to observe anisotropy of the photoconductivity on the crystals with ordered stoichiometric vacancy and high tetragonal compression. The observed dependencies are rather complicated and may depend on the nature of the lattice defects and also on presence of close lying energies of the optical transitions that have different selections rules

Our study of the azimuthal dependencies of photoconductivity i_ϕ of the CdGa₂S₄ and HgGa₂S₄ single crystals allow to establish that the positive the native photopleochroism coefficient in the crystals with ordered vacancy exhibit variation along the photoacceptance plane, while the azimuthal angles for maximum and minimum values of the photocurrents are sufficiently well reproducible by scanning the exciting light position along the whole (100) plane.

The positions of maximums and minimums in the photocurrent excitation zones corresponds to the main crystallographic axes [100] and [001]. We suppose that observed the spread of the positive the native photopleochroism is connected with fluctuations on the character of positional ordering of atoms in the HgGa_2S_4 CdGa_2S_4 single crystals.

The analysis of the observed results allows to formulate that for the clarification of the reasons that cause inversion of the sign the native photopleochroism coefficient in the CdGa_2S_4 and HgGa_2S_4 compounds it is need first of all to suppress the influence of the surface recombination of the photogenerated charge carriers to the photoconductivity processes. It is evident, that the one of the most effective ways to solve this problem may be creation of the photosensitive structures the CdGa_2S_4 and HgGa_2S_4 compounds.

The problem of creation of the photosensitive structure on the base of $n\text{-HgGa}_2\text{S}_4$ crystals is solved and investigations of the photoelectrical properties have been performed. The main photoelectrical parameters of the structures determined indicate on high efficiency of photoconversion in the wide spectral range of 0.9-3.8 eV. It is shown that the surface-barrier structures on the base of $n\text{-HgGa}_2\text{S}_4$ single crystals can find different applications in photoelectronics of highly desired shortwavelength spectral range.

9. Current technical status

- on schedule, behind, ahead
All works are on schedule.
- refining next year schedule if necessary
- recommendation for changes of the work plan, if necessary

10. Cooperation with foreign collaborators

- exchange of scientific material (information, computer codes and data, samples)
We present 2nd year annual report.
- signature of protocols (with short description)
- research carried out jointly
- trips to/from foreign collaborators
- workshops, topical meetings organized by the project team
- joint attendance to international conferences

11. Problems encountered and suggestions to remedy

12. Perspectives of future developments of the research/technology developed

Our study with development of different optical and electrical research techniques show a new perspectives and opens up new approaches for better understanding the band structure of chalcopyrite crystals and structures on their base.

Attachment 1: Illustrations attached to the main text

Attachment 2: Other Information, supplements to the main text

Attachment 3: Abstracts of papers and reports published during the year of reference

Attachment 4: Information on patents and property rights.

III. ATTACHMENTS

III. Summary of personnel commitments for the 2d year

Category I – 245 days and Category II – 325 days.

IV. Equipment acquired during the year.

No equipment was acquired.

7. Technical progress during the 3d year

According to the Work Plan we have conducted the Task 5:

Polarized photosensitivity measurements (in a temperature range from 77 to 300K) of surface barriers on In/CdGa₂S₄ and In/HgGa₂S₄.

We have performed investigations of the contact phenomena of photosensitive surface-barrier structures on the base of the CdGa₂S₄ single crystals with n-type conductivity. We study the stationary and light current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion in dependence of the geometry of excitation with a unpolarized irradiation.

The main efforts of our experimental search was devoted toward study of electrical properties and optical absorption of the CdGa₂S₄ single crystals, study of contact properties of these crystals with some metals such as In, Au, Cu, Ni, and Ag with aim to reveal the possibilities of fabrication surface-barrier structures and measurements of the spectral dependencies of quantum efficiency of photoconversion. We have observed photovoltaic effect of the surface-barrier structures studied stationary and current-voltage characteristics as well as the spectra of quantum efficiency of the photoconversion.

Our main results are following:

1. For our study we have used the CdGa₂S₄ single crystals grown without preliminary doping by different impurities using two different techniques:
 - I) by horizontal crystallization from the melts close to the stoichiometric for ternary compounds,
 - II) by gasphase transport reactions.

From the measurements of the kinetic coefficients we established that without doping both techniques allows to obtain samples that showed n-type conductivity with very high specific electrical resistance $\rho \approx 10^9 - 10^{10} \Omega \cdot \text{cm}$ at $T = 300\text{K}$. The most high-ohmic samples are obtained by the gasphase crystallization technique. Estimations on the base of our measurements give the following values for the concentration $n \approx 10^8 - 10^9 \text{ cm}^{-3}$ and mobility $\mu_n \approx 1-10 \text{ cm}^2/(\text{B c})$ at $T=300 \text{ K}$. At the temperatures lower than the room

temperature rapid increase of ρ does not allow to carry out temperature dependent measurements of $\rho(T)$ and $n(T)$.

2. Figure 1 shows spectrum of optical absorption ($\alpha\hbar\omega$) for one of the n -CdGa₂S₄, on which was performed experiments on creation of the photosensitive structures. The beginning of an increase of the optical absorption at $\hbar\omega > 2.8$ eV can be used for estimation of the energy band gap of the n -CdGa₂S₄ single crystals. As seen in the Fig. 2, in the coordinates of $(\alpha\hbar\omega)^{1/2} - \hbar\omega$ the $\alpha(\hbar\omega)$ the spectrum exhibits linear behavior, which by taking into account the theory of the interband optical transitions in semiconductors [1] can be interpreted as the indirect interband optical transitions in the n -CdGa₂S₄ single crystals grown by the both crystallization techniques used.
3. We have established that mechanical contact of pure metal layers of (In, Ag and Cu) with the cleaved surface of the CdGa₂S₄ single crystals as well as with freshly cleaved surface of the electrically homogeneous CdGa₂S₄ independently of the growth techniques used, show sharp rectifying characteristics (Fig. 3). The maximum value of the rectification was obtained when In as a barrier contact was used. The maximum value of the rectification coefficient determined as ratio of the direct current to the reverse current at the fixed value of the bias $U \approx 10 - 20$ V, reaches the values $K \approx 15$ at $T = 300$ K.

In the bias range $U > 10 - 15$ V the current-voltage characteristics follow to the linear law

$$I_{\text{dir}} = (U - U_0) / R_0, \quad (1)$$

Where the residual resistance without illumination of the structure $R_0 \approx (3-5) \cdot 10^8 \Omega$ at $T = 300$ K. The falls up to $R_0 \approx (6-8) \cdot 10^5 \Omega$. The reverse current at the bias $U \approx 5$ V $I_{\text{rev}} \sim U_{\text{rev}}^\gamma$, where $\gamma \approx 1.1$ in the range $U_{\text{rev}} < 10$ V and increases with increasing of the reverse bias. This value indicate influences of the nonperfect periphery of the first structures and solving the problems of their doping may allow further essential improvement of the surface-barrier structure characteristics on the base of n -CdGa₂S₄.

4. Under illumination of the surface-barrier structures on the base of n -CdGa₂S₄ the observed photovoltaic effect is connected with formation at the interface of the metal/semiconductor of potential barrier that cause the separation of the was also observed. The sign of photovoltage of the free motion in the surface-barrier structures on the base of n -CdGa₂S₄ single crystals always corresponded to the negative potential on the semiconductor. In this case, the sign of the photovoltage is independent on the energy of incident photons, intensity of radiation, as well as localization of light beam at the surface of illumination structure. Therefore, the photosensitivity the structures developed is determined by the photovoltaic processes in the single energy barrier connected with the contact of semiconductor and metal studied. Maximum value of the voltage photosensitivity achieved for the surface-barrier In- n -CdGa₂S₄ structures is 100 V/W at $T = 300$ K. Some of the typical spectral dependencies of the relative quantum efficiency of photoconversion η for the surface-barrier n -CdGa₂S₄ structures are given in the Fig. 4 and Fig. 5. It is well seen that under conditions of illumination from the barrier contact side the photosensitivity is observed in the wide spectral range of 1 – 4 eV. The spectra $\eta(\hbar\omega)$ are located in the short wavelength range $\hbar\omega > 2.2$ eV only in the case if as the substrate for the barriers used the n -CdGa₂S₄ crystals grown from the melt (Fig. 4 and Fig. 5). The latter can be induced by the higher value of defect concentration and, consequently, by absorption in the crystals obtained from the gas phase. The spectral dependencies $\eta(\hbar\omega)$ of the surface barrier structures are very complicated (Fig. 4 and

Fig. 5). They contain many broad structures, maximum energy position of which and the values of the photoconversion strongly changes from structure to structure at $\hbar\omega < 2.7$ eV. For the many structures obtained on the base of the CdGa_2S_4 crystals grown from the melt close to the stoichiometric at the photon energy range $\hbar\omega > 2.8$ eV there exist sharp maximum at $\hbar\omega = 3.67$ eV that coincides with the energy of the direct interband transitions in this compound [3-5]. Note that some of these structures in the spectra $\eta(\hbar\omega)$ of the surface-barrier $\text{In-}n\text{-CdGa}_2\text{S}_4$ structures were observed in the studies of the energy spectra of local states in this semiconductor by other authors [6-8]. The nature of these levels is not understood yet. Clarification of the situation requires detail analyze and revealing connections between these structures in the $\eta(\hbar\omega)$ spectra and growth conditions of growth as well as thermal treatments of the CdGa_2S_4 crystals. Observed different features in the $\eta(\hbar\omega)$ spectra of the investigated structures give base to consider application of the photoactive absorption spectroscopy for study energy spectra of local states, and, consequently, of crystal perfection of CdGa_2S_4 .

5. So, for example, as seen from Fig. 5 in the surface-barrier structures obtained on the base of gasphase CdGa_2S_4 crystals using the same technology conditions at the photon energy range $\hbar\omega > 2.8$ eV in the η spectra always appears sharp cut-off of the photosensitivity that does not allow to study photosensitivity in the range of the direct optical transitions in this semiconductor. At the same time, from the Fig. 5 one may conclude that the contribution to the photoactive absorption in the impurity range for the sample grown by gasphase is higher than for the same type of surface-barrier structures for the samples obtained from the melt close to the Stoichiometric.

Our analyze shows that the long wavelength edge of the $\eta\hbar\omega$ spectra of the surface-barrier structures follows to the Fowler law that allows to connect it with photoemission of electrons into the semiconductor. From the extrapolation of the long wavelength part $\eta^{1/2} \rightarrow 0$ allows to obtain the energy height of $\text{In-}n\text{-CdGa}_2\text{S}_4$ structures $\varphi_B \approx 1.2\text{eV}$ at $T=300$ K. Similar values of φ_B were obtained for the surface-barrier structures with Au and Cu layers.

5. So, in our work, the problem of creation of the photosensitive structures on the base of $n\text{-CdGa}_2\text{S}_4$ crystals is solved and for the first time investigations of the photoelectrical properties have been performed. Our experimental results on the firstly obtained structures allow determining the main photoelectrical parameters of the structures as well as properties of new ternary CdGa_2S_4 semiconductor compound. It is established that the surface-barrier structures on the base of $n\text{-CdGa}_2\text{S}_4$ single crystals allow photogeneration in the wide spectral range of 1- 4 eV due to such a different on the nature processes as photoemission of nonequilibrium current carriers, optical transitions with participation of local states and interband indirect and direct optical transitions. As a result, it is also shown that the surface-barrier structures on the base of CdGa_2S_4 single crystals are interesting for different device applications for the short wavelength photoelectronics.

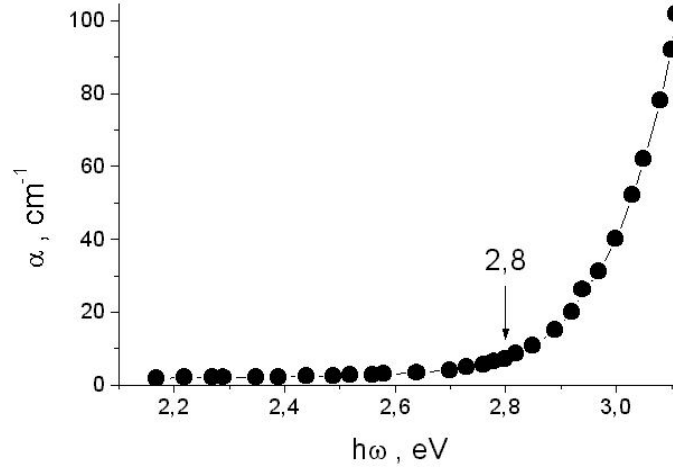


Fig. 1. Spectral dependence of the optical absorption coefficient for the CdGa_2S_4 single crystal at $T=300$ K in nonpolarized light (Sample No.11K grown from the melt. Thickness of the plate $d \approx 0.5$ mm).

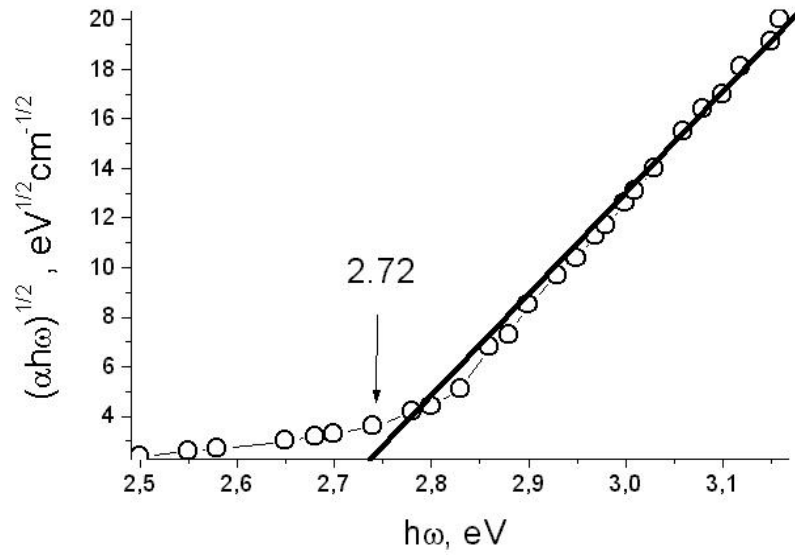


Fig. 2. Spectral dependence of the optical absorption coefficient in the coordinates of $(\alpha\hbar\omega)^{1/2} - \hbar\omega$ for the CdGa_2S_4 single crystal at $T=300$ K. (Sample No.11K Vertical arrow indicate the extrapolated value of photon energy).

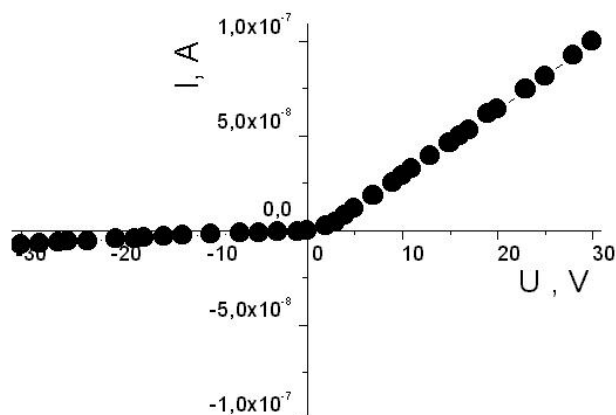


Fig. 3. Stationary current-voltage characteristic of In-*n*-CdGa₂S₄ surface-barrier structure at $T=300$ K (Sample 17K grown from the melt. Transmission direction is realized at the external positive bias at the barrier contact.).

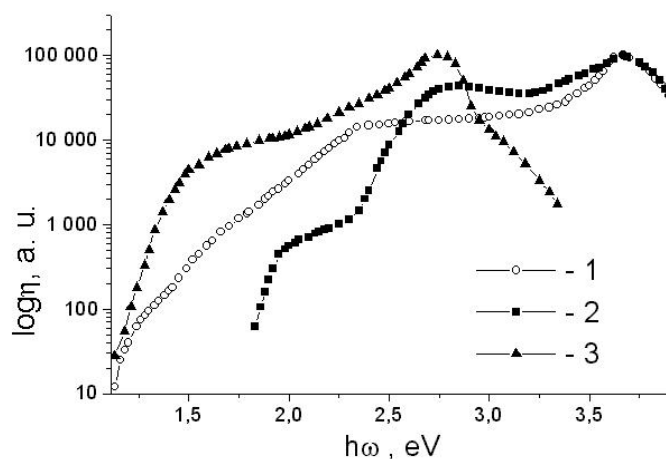


Fig. 4. Spectral dependencies of the relative quantum efficiency of photoconversion for the surface-barrier In-*n*-CdGa₂S₄ structures at $T=300$ K in the nonpolarized radiation (Sample No.17K – curve 1, Sample No.19B – curve 2, Sample No.34SP – curve 3. The crystal is grown from the gasphase).

References

1. Yu.I. Ukhonov. Opticheskie svoistva poluprovodnikov (Nauka, Moscow, 1977).
2. S.M. Sze. Physics in Semiconductor Devices (A Wiley-Interscience publ., N.-Y., 1981).
3. A.K. Georgobiani, S.I. Radauzan, and I.M. Tiginianu. Semiconductors, **19**, 193 (1985).
4. A.G. Areshkin, V.F. Jutar', I.M. Tiginianu, V.Ia. Reilian, and L.G. Suslina. Semiconductors, **13**, 337 (1979).
5. A.K. Georgobiani, Yu. V. Ozerov, S.I. Radauzan, and I.M. Tiginianu, Solid Stsate Physics, **23**, 2094 (1981).
6. P. Kivits, M. Wijnaker, J. Glasson, J. Geerts. J. Phys. C: Sol.St/Phys., **11**, 2361 (1968).
7. A.N. Georgobiani, A. N. Gruzinzhev, I.M. Tiginyanu. Kratkije Soobshenia po Phizike PhI Lebedev, No2, 3 (1981).
8. A.N. Georgobiani, S.I. Radautsan, I.M. Tiginyanu. Phys. St. Sol.(a), **69**, 513 (1982).

According to the Work Plan we have conducted the Task 5:

Polarized photosensitivity measurements (in a temperature range from 77 to 300K) of surface barriers on In/CdGa₂S₄ and In/HgGa₂S₄.

We have performed investigations of the spectral dependencies of polarized photosensitivity of surface-barrier structures In-n-CdGa₂S₄ and In-n-HgGa₂S₄ in the temperature range 77-300K.

C) Milestones Completed

The main efforts of our early experimental search was devoted toward the study of polarized photoluminescence (task 3) and stationary photosensitivity of homogeneous n-CdGa₂S₄ and n-HgGa₂S₄ single crystals. These pioneer investigations has allowed for the first time to analyze the anisotropy of the optoelectronic processes in such materials. However these experiments due to the influence of the surface recombination of photogenerated pairs and not sufficient perfection of these semiconductors do not allowed to observe the anisotropy of the photoactive absorption in the range of fundamental optical transitions of the CdGa₂S₄ and n-HgGa₂S₄ single crystals. Keeping in mind this aim we have obtained wideband-photosensitive structures of CdGa₂S₄ and HgGa₂S₄ (Task 5, Q9 and 10), that opened new possibilities for the first time to study photopleochroism [1] in crystals with ordered vacancy.

The main results of the first investigations of the polarized measurements of the photosensitivity of surface-barrier structures In-n-CdGa₂S₄ and In-n-HgGa₂S₄ are following:

1. Our study of the photosensitivity of the surface-barrier structures In-n-CdGa₂S₄ and In-n-HgGa₂S₄ created on the oriented surfaces (100) and (001) on CdGa₂S₄ and HgGa₂S₄ wafers, has revealed the observation of the laws, characteristic for the anisotropic semiconductors in dependencies of the shortage current on the orientation of the vector of the electric field of the light wave relative to the tetragonal axes c of the preliminarily undoped CdGa₂S₄ and HgGa₂S₄ ternary compounds. Under conditions of illuminating such a structures by the linearly polarized radiation along the normal to the acceptance surface (001), the shortage photocurrent, as a rule, does not depended on the space orientation of E . If one shines the structures from the acceptance surface (001), the photocurrent revealed the periodic dependence on the azimuthal angle between E and c , which known as the Malluse law [1]. These dependencies allow to make important conclusion that anisotropic semiconductor compounds CdGa₂S₄ and HgGa₂S₄ with ordered stoichiometric vacancy show the phenomenon of the native photopleochroism, and azimuthal dependencies for the surface-barrier structures correspond to the symmetry of unit cell of these compounds.
2. We have obtained the spectral dependencies of the relative quantum efficiency of photoconversion $\eta(h\nu)$ of the oriented surface-barrier structures In-n-CdGa₂S₄ and In-n-HgGa₂S₄. Under conditions of illumination of of surface-barrier structures In-n-CdGa₂S₄ from the side of semitransparent barrier layer in ($d=0.1$ mm) along the normal to the (001) surface CdGa₂S₄, the longwavelength edge of the relative quantum efficiency of photoconversion $\eta(h\nu)$ in the range of indirect interband transitions exhibit the same polarization dependence as the coefficient of the optical absorption of the CdGa₂S₄. The dependence in the temperature range 80-300 K is connected with shift of the long wavelength part of the spectra $\eta(h\nu)$ to the short wavelength part of the spectra with the transition from the polarization $E \parallel c$ to $E \perp c$, why the inequality $\eta > \eta^\perp$ is satisfied. Such an inequality is achieved for the In-n-CdGa₂S₄ structures, that fulfill the correspondence between the processes of optical absorption and photo conversion in the range of high absorption. Polarization splitting of the $\eta(h\nu)$ spectra is $\approx 70 - 80$ meV and may be due

to the lifting of the degeneracy in the free zone due to the high natural tetragonal distortion of the CdGa_2S_4 crystal lattice.

In the range of indirect interband transitions in the CdGa_2S_4 the coefficient of natural photopleochroism P_N is positive and reach the maximum $\approx 50\%$ near the photon energy $hw \approx 2.75$ that is close to the energy of the interband transitions of the CdGa_2S_4 crystals (Fig. 1).

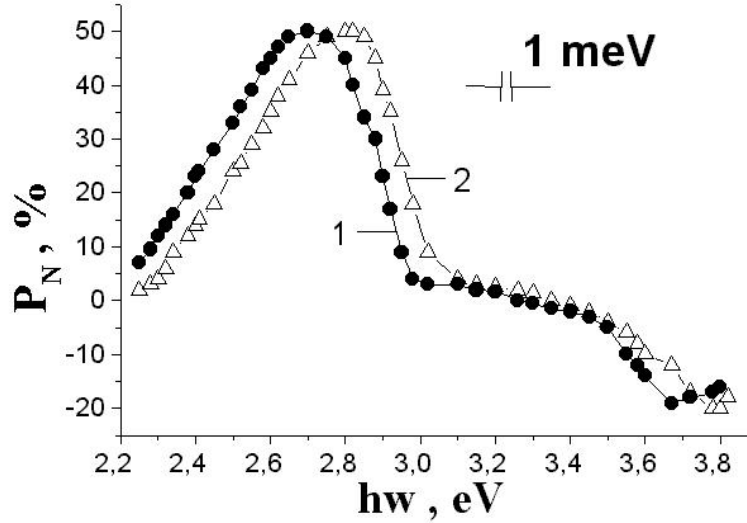


Fig. 1. The coefficient of natural photopleochroism in the range of indirect interband transitions of the surface-barrier structures In-n- CdGa_2S_4 at room temperature (1) and 80 K (2). The illumination of the structure is from the side of the barrier contact. The illumination surface of the CdGa_2S_4 is (100).

With increase of the photon energy in the range $hw > 2.9$ eV the coefficient of natural photopleochroism in the temperature range 80-300 K is fall down and is kept rather low ($P_N \approx 2-5\%$) until 3.4 eV that may be the result of concurrence between optical transitions with other side selection rules. And only with approaching to the energy of direct interband transitions $E_G^{dir} \approx 3.7$ eV ($T=300$ K) is became an increase of the amplitude of the negative photopleochroism coefficient up to $\approx 20\%$. This experimental fact means that the direct interband transitions in the CdGa_2S_4 single crystals mainly are allowed in the $\mathbf{E} \perp \mathbf{c}$ polarization. Because there is not detailed theoretical calculations of the band structures CdGa_2S_4 single crystals it is impossible to perform a comparison.

It is important to note, that reduction of the temperature in the range from 300 to 80 K the spectral shape of the photopleochroism coefficient does not exhibit any changes, but only a shifts to the short wavelength range with a speed of $\approx 4 \cdot 10^{-4}$ eV/K that is typical value for tmperature shift of the band gap for diamond like semiconductors [5].

The absence of the notable changes in th $P_N(hw)$ spectrum and of the values of the P_N allows to conclude about the absence of a phase transitions in the CdGa_2S_4 in the temperature range 80-300 K.

3. We have obtained $\eta(hw)$ spectra of the In-n- HgGa_2S_4 , structures on oriented n- HgGa_2S_4 single crystals. Increasing of the photon energy up to $hw \approx 2.3$ eV of the (100) oriented surface-barrier structures In-n- CdGa_2S_4 and In-n- HgGa_2S_4 leads to $\eta > \eta^\perp$ and to positive sign of $\Delta \eta = \eta - \eta^\perp$. And further, at the definite value of the photon energies the

$\Delta \eta$ crosses 0 and (photoisotropic point) and then in the range 2.4 – 3.8 eV is negative. This situation is the same for all obtained our In-n-HgGa₂S₄ structures.

Our analyze of $\eta(h\nu)$ for linearly polarized radiation has shown that characteristic for the indirect optical transitions dependencies $(\eta \perp h\nu)^{1/2} = f(h\nu)$ are less sensitive to the polarization and their extrapolation to the 0 gives equal for both polarizations the value of $E_G^{in} \approx 2.28$ eV ($T=300$ K), which is obtained from the analyze of the photosensitivity spectra for the unpolarized radiation. Transition from the polarization $\mathbf{E} \perp$ to $\mathbf{E} \parallel \mathbf{c}$ practically causes parallel shift of the $\eta(h\nu)$ spectra to the short wavelength range of ≈ 80 meV. The analyze of these dependencies $(\eta \perp h\nu)^2 = f(h\nu)$ has allowed to determine direct band gap $E_G^{nir} \approx 2.87$ eV ($T=300$ K) for $\mathbf{E} \perp \mathbf{c}$ polarization and $E_G^{nir} \approx 2.95$ eV for polarization $\mathbf{E} \parallel \mathbf{c}$. The reduction of the temperature in the range from 300 to 80 K the the grows of these parameters take plays with a speed of $\approx 4 \cdot 10^{-4}$ eV/K for the both polarizations of the incident radiation.

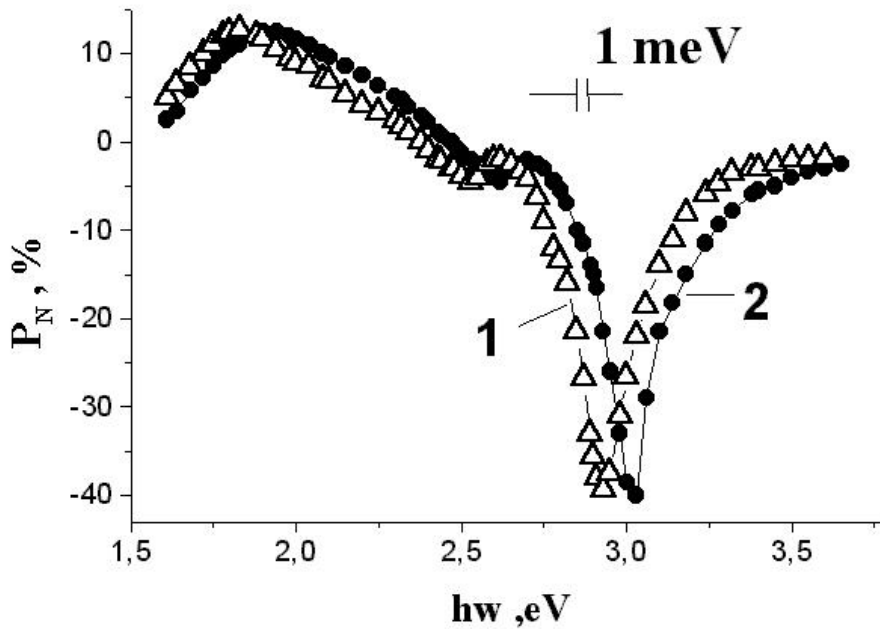


Fig. 2. The coefficient of natural photopleochroism in the range of indirect interband transitions of the surface-barrier structures In-n-HgGa₂S₄ at room temperature (1) and 80 K (2). The illumination of the structure is from the side of the barrier contact. The illumination surface of the HgGa₂S₄ is (100)

Fig. 2 shows the coefficient of natural photopleochroism in the range of indirect interband transitions of the surface-barrier structures In-n-HgGa₂S₄ at room temperature and 80 K. It is seen that reduction of the temperature practically does not influence to the shape of $P_N(h\nu)$ spectra, but causes their shift to the short wavelength range with the same speed that was determined for the direct interband optical transitions. The sign of the P_N is positive only in the range of the nonintrinsic absorption of the n-HgGa₂S₄ crystals at $h\nu < 2.3$ eV, while its inversion is observed with transition to the short wavelength range $h\nu > 2.5$ eV. The maximum of the negative coefficient of natural photopleochroism P_N is reached as in the case of the CdGa₂S₄ crystals at energies close to the energy of the E_G^{nir} . The same was early observed for the pseudodirect ternary A^{II}B^{IV}C^V₂ compounds with the chalcopyrite structure [1,6].

4. In conclusion, for the first time for the surface-barrier structures created on oriented single crystals of ternary compounds with ordered stoichiometric vacancy CdGa_2S_4 and HgGa_2S_4 we have obtained spectra of the relative quantum efficiency of photoconversion for the linearly polarized radiation in the temperature range 77-300K.

$\eta(h\nu)$ in the range of indirect interband transitions exhibit the same polarization dependence as the coefficient of the optical absorption of the CdGa_2S_4 . The dependence in the temperature range 80-300 K is connected with shift of the long wavelength part of the spectra $\eta(h\nu)$ to the short wavelength part of the spectra with the transition from the polarization $\mathbf{E} \parallel \mathbf{c}$ to $\mathbf{E} \perp \mathbf{c}$, why the inequality $\eta > \eta_{\perp}$ is satisfied.

In conclusion, development of the polarized photoelectrical spectroscopy allowed for the first time to obtain photactive absorption in the range of direct interband transitions, to determine the energy and temperature coefficients for this transitions, as well as to observe the phenomenon of the natural photopleochroism. Our study revealed the possibility of application of the CdGa_2S_4 and HgGa_2S_4 in the polarized photoelectronics for the highly desired shortwavelength spectral range and demonstrated the further need for development of technological investigations on improvement structural perfection and sizes of these single crystal compounds.

References

9. F. P. Kesamanly, V. Yu. Rud' and Yu. V. Rud', Semiconductors 33, 513, (1999).
10. A.K. Georgobiani, S.I. Radauzan, and I.M. Tiginianu. Semiconductors, **19**, 193 (1985).
11. V. L. Panukhin, B. E. Ponedelnikov, L. E. Rozenson, and V. I. Chijikov, Izv. Vbuzov, Ser. Physics, **22**, 57 (1979).
12. F.M. Gashimzade, D. A. Guseinova, V. I. Shtensraiber, Raschet zonnnoi struktury tiogallatov kadmia metodom LKAO, Preprint #21, Baku, IFAN Az SSR, 1980, 20p.
13. Fiziko-khimicheskie svoistva poluprovodnikov, ed. A. V. Novoselova, Moscow, Nauka, 1978.
6. Yu. V. Rud', Izv. Vuzov SSSR, Ser, Fizika, 29, 68 (1986)

According to the Work Plan we have conducted the Task 6:

Temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of CdGeAs_2 for determination mobility, concentration, activation energy of impurity level, and degree of compensation.

We have performed temperature dependent measurements of Hall-effect coefficients and electrical conductivity (in the range of 77-300 K) measurements of CdGeAs_2 grown by low temperature crystallization.

The main efforts of our early experimental search were devoted toward the study of polarized photoluminescence and stationary photosensitivity of homogeneous $n\text{-CdGa}_2\text{S}_4$ and $n\text{-HgGa}_2\text{S}_4$ oriented single crystals. These investigations have allowed for the first time to analyze the anisotropy of the optoelectronic processes in such materials.

High values of resistance and low values of free carriers that are realized by using modern growth technologies do not allow performing detailed temperature dependent measurements of the kinetic coefficients – electroconductivity σ and Hall coefficient R . Therefore, for study temperature dependencies of the above kinetic coefficients we have measured another ternary anisotropic compound - CdGeAs_2 with the chalcopyrite that is very close to the structure of $n\text{-CdGa}_2\text{S}_4$ and $n\text{-HgGa}_2\text{S}_4$ crystals with the structure of

ordered stoichiometric vacancy. And for this CdGeAs₂ crystal we have measured temperature dependencies $\sigma(T)$ and $R(T)$.

For our measurements CdGeAs₂ crystals were grown by low-temperature crystallization from solutions-solvents. All CdGeAs₂ crystals, grown by this technique, had well-developed shapes, characteristic for chalcopyrite compounds (space group D_{2d}¹² [1]). Our x-ray diffraction measurements have shown that within the accuracy of the measurements the lattice parameters are close to CdGeAs₂, grown at the crystallization temperature close to the stoichiometric ternary compound CdGeAs₂ melt [1,2].

Measurements of kinetic parameters are performed on the samples with dimensions of $\sim 0.1 \times 0.3 \times 5 \text{ mm}^3$ in the low constant electric and magnetic fields ($E \leq 1 \text{ V/cm}$, $H \leq 5 \text{ ke}$). Current contacts to such a small samples were prepared by welding of pure indium and potential contacts were created by electric discharge with 50 μm diameter platinum wires near the mechanically and chemically polished surfaces of the CdGeAs₂ crystal surfaces. Connections of the wires were made without destroying surface quality of the crystal. The quality of such contacts were sufficiently high and withstand thermal cycling at the temperature range 300-77 K. Measurements of the potentials were performed by compensating technique.

The accuracy of measurements of the kinetic coefficients – electroconductivity σ and Hall coefficient R nor exceeded 3 and 5%, respectively.

Our measurements have shown that used growth technique of the CdGeAs₂ crystals allows to obtain electrically uniform samples with n-type conductivity without preliminary doping.

Table 1 demonstrate the size of electrically homogeneous samples and measured values of electroconductivity σ and Hall coefficient R nor exceeded 3 and 5%, respectively at $T = 300$ and 77 K. The spread of the values of the potential at the zounds were not exceeded 3%.

Table 1.

Electrical properties of *n*-CdGeAs₂ crystals at $T = 300$ and 77 K.

No	Dimensions	300 K		77 K	
	Mm	σ $\Omega^{-1} \cdot \text{cm}^{-1}$	R cm^3/Q	σ $\Omega^{-1} \cdot \text{cm}^{-1}$	R cm^3/Q
1π	0.12x0.25x4.5	2950	3.85	5000	6.83
3π	0.20x0.40x5.0	2830	3.53	5120	6.60
4π	0.23x0.35x5.5	2760	3.61	5100	6.51
5π	0.15x0.32x4.2	2870	3.35	5200	6.35
7π	0.17x0.30x3.0	2580	3.88	4900	6.53
10π	0.11x0.25x4.1	2820	3.55	4980	7.03

Note, that samples grown by the generally used technique of direct crystallization close to the stoichiometric ternary compound CdGeAs₂ melt show only *p*-type conductivity and high electric inhomogeneity [3]. As a result at the nitrogen temperatures measurements of the Hall coefficients became impossible due to the coexistence of areas with *n*- and *p*-type

conductivity. The high electrical conductivity indicated also by a very low magnetoresistance (less than 0.01 % at magnetic fields up to 15 kG).

Therefore, by extrapolating obtained results to the $A^{II} B^{III}_2 C^{VI}_4$ compounds it is possible to conclude that such properties as

- i) low concentration of free carriers,
- ii) low mobility of charge carriers,
- iii) noncontrolled type of conductivity, and
- iv) existence of deep levels,

need to connect with the fact that currently used technique does not allow to solve needed in such cases problem of control the deviations from the stoichiometry that is the main reason of observed fixed level of semiconductor parameters of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals.

One of the most actual technology directions of the $CdGa_2S_4$ and $HgGa_2S_4$ crystals is to find new ways of considerable reduction of a crystallization temperature of these ternary chalcogenides that will allow to decrease concentration of the lattice defects of nonstoichiometric nature.

Typical temperature dependences $R(T)$ and $\sigma(T)$ for one of the sample is shown in Fig.1.

Figure 2 shows typical experimental temperature dependence for Hall mobility $\mu_n(T)$ and in Fig. 3 we present comparison of experimental data with calculated results $\mu_n(T)$ for different scattering mechanisms.

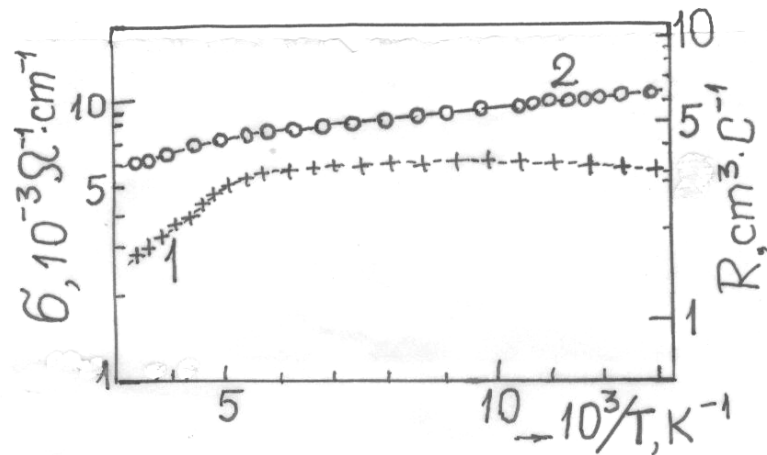


Fig.1. Temperature dependences for specific conductivity (curve 1) and hall coefficients (curve 2) for n-CdGeAs₂ single crystal sample grown by low temperature crystallization (Sample 10n).

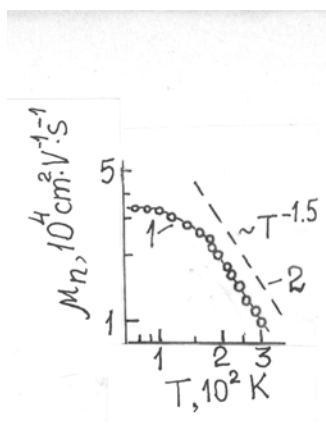


Fig.3. Experimental Temperature dependences for Hall mobility $\mu_n(T)$ (curve 1) for n-CdGeAs₂ single crystal sample grown by low temperature crystallization (Sample 10n). Theoretical data $\mu_n(T)$ (curve 2) calculated for the case of the scattering by lattice vibrations.

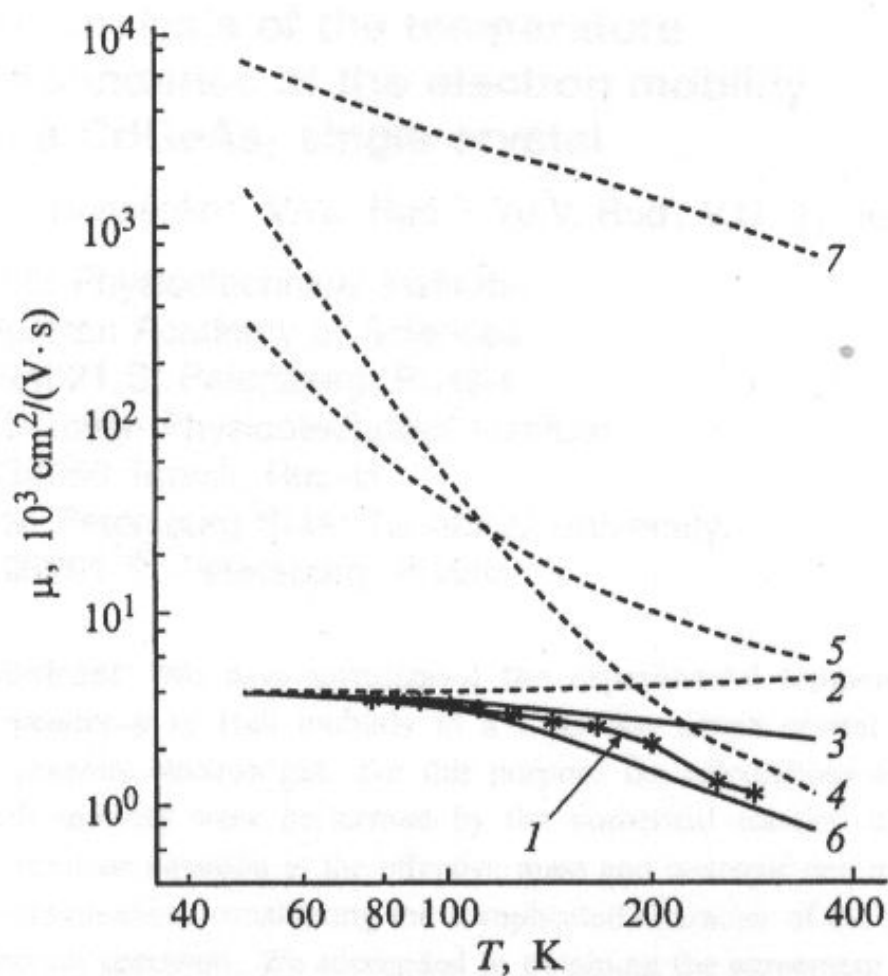


Fig.3. Experimental (curve 1) and calculated dependences $\mu_n(T)$ for n-CdGeAs₂ single crystal sample calculated for the case of the scattering: on impurity ions (curve 2), ions and polar optical phonons (curve 3), plasma vibrations (curve 4), polar optical phonons (curve 5), ions, polar optical phonons and plasma vibrations (curve 6), and acoustic vibrations (curve 7).

III. ATTACHMENTS

V. Summary of personnel commitments for the 3d year

Category I – 212 days and Category II – 303 days.

VI. Equipment acquired during the year.

No equipment was acquired.

IV. SIGNATURES

Deputy Director

Ioffe Physico-Technical Institute



V. A. Dergachev

Project Manager



Yu. V. Rud'

08/31/04